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CV.—*The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part II. Products Derived from α-Halogenated Adipic Acids.*

By Christopher Kelk Ingold.

In Part I of this series (this vol., p. 305) a wide range of facts relating to the formation of carbon rings was briefly reviewed in the light of the hypothesis that the spatial configuration of four atoms attached to a central carbon atom is determined by their relative volumes, and it was shown that many of the more apparent defects of the Baeyer strain theory may easily be rectified by means of this simple assumption.

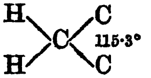
The main points regarding which Baeyer's theory is open to objection fall into two classes, the first consisting of those which relate to the number of carbon atoms forming the ring, the second those relating to the effect on ring formation of the presence of substituent groups.

Regarding the former, it was calculated that the angle between the valencies connecting two carbon atoms to the carbon atom of an unstrained methylene group is, not 109·5°, but 115·3°, and that the figures representing the difficulty attending the formation of a *cyclo*propane ring from a *n*-propane chain and of *cyclo*butane, *cyclo*pentane, and *cyclo*hexane rings from the corresponding normal carbon chains were as follows:

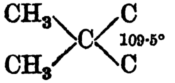
*cyclo*Propane.	*cyclo*Butane.	*cyclo*Pentane.	*cyclo*Hexane.
0·345	0·427	0·220	0·207.

Whilst these numbers were in excellent functional agreement with thermochemical data and with general experience of the production of ring compounds, particularly with experiments indicating the difficulty attending the closure of the *cyclo*butane ring as compared with the *cyclo*propane ring and the almost equal ease of formation of five- and six-membered carbon rings, it was felt to be desirable, especially as in these respects the new hypothesis is definitely in conflict with the deductions of Baeyer's theory, to institute a special series of truly comparative experiments in which, by employing uniform experimental conditions and by utilising the principle of the standard side-reaction (*loc. cit.*, p. 310), the adventitious influences, which so seriously detract from the value of the conclusions drawn from incidental observations, could to a very large extent be eliminated.

With regard to the influence of substituent groups on ring formation, it was pointed out that the most uniform and the most frequently exhibited effect of this kind is that of the *gem*-grouping in promoting the formation of three-, four-, and five-carbon rings, an effect which may be explained in a very simple manner if it be true that two carbon atoms associated with a *gem*-grouping (*B*) are in closer proximity than two carbon atoms attached to a methylene group (*A*).



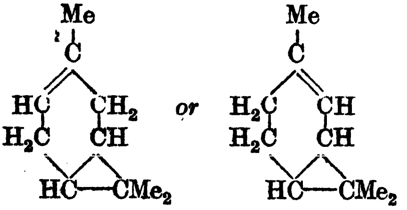
(*A*.)



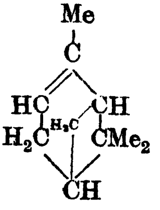
(*B*.)

The reality of the phenomenon cannot be doubted. There are on record numerous examples (*loc. cit.*) of synthetical experiments in which the effect of the *gem*-dialkyl group on ring closure is clearly manifested. Apart from synthetical experiments, however, there is another quarter from which confirmation of a very significant character is forthcoming, namely, the chemistry of natural products.

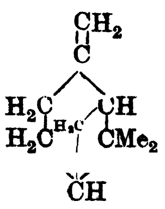
It is well known that the types of ring which occur most frequently in nature are those composed of five or of six atoms. There is one class of natural products, however, the essential oils, in which many of the compounds contain carbon rings of the more highly strained types, and it is of interest to observe the manner in which in these cases the strains inherent in the type of ring (*cyclo*propane and *cyclo*butane, for example) are relieved by the entrance of the *gem*-grouping or some equivalent arrangement into the constitution of the substance. Thus in every case in which there exists in a naturally occurring product a *cyclo*propane ring there exists also, either an attached *gem*-dimethyl group, as in the case of carene (Simonsen, T., 1920, **117**, 571) or some equivalent arrangement involving quaternary carbon, as with thujone and sabinene. Where there occurs a substance containing a *cyclo*butane ring, a *gem*-dimethyl group is invariably attached to it, as, for example, in α- and β-pinene :



Carene.

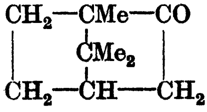


α-Pinene.

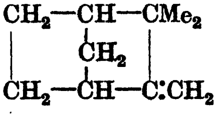


β-Pinene.

Naturally occurring, five-membered rings, on the other hand, in some cases carry a *gem*-grouping and in others do not. Thus, whilst camphor contains two *cyclo*pentane rings having a *gem*-grouping common to both, camphene also possesses two *cyclo*pentane rings, only one of which is furnished with a *gem*-group :



Camphor.



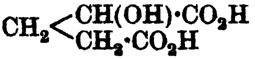
Camphene.

Finally, it must be noticed that of all the naturally occurring, six-membered rings known in terpene chemistry not one bears a *gem*-dialkyl group. Every cyclic carbon atom in limonene, α-terpineol, sylvestrene, pulegone, α-phellandrene, β-phellandrene, and carvone, to take a few of the better known examples, is either secondary or tertiary.

These facts are obviously in complete agreement with the hypothesis suggested in Part I. *cyclo*Propane and *cyclo*butane rings are clearly those which most require the introduction of the *gem*-dimethyl group in order to render them sufficiently stable to be capable of occurrence in nature. Since the angle (108°) of a *cyclo*pentane ring is smaller than the normal angle (115·3°; *loc. cit.*), this ring also is stabilised and rendered easier of formation by the introduction of the *gem*-dimethyl group. The reverse, however, is the case with the *cyclo*hexane ring, and it is therefore significant that *gem*-dimethyl groups do not appear to be supplied to *cyclo*hexane rings in nature.

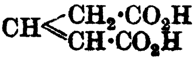
The completeness with which such a remarkable diversity of facts are collated by the hypothesis which forms the basis of this series of papers gave birth to the conviction that it was extremely desirable to test the matter by every possible means, and one essential step appeared to be to make a determination of the relative ease of formation of *cyclo*propane and *cyclo*butane rings by the method outlined in Part I.

In Part I the action of alkalis on α-halogenated glutaric acids under two sets of experimental conditions was described. The general conclusion was drawn that, whilst with dilute alkalis (conditions *A*, this vol., p. 318) almost the whole of the material underwent the standard side-reaction and became converted into the corresponding hydroxy-acid (I), with concentrated alkali (conditions *B*, p. 319) about 50 per cent. of the *cyclo*propane derivative (III) was produced together with the hydroxy-acid (I) and a trace of glutaconic acid (II).



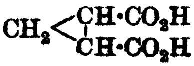
$$CH_2<\begin{matrix}CH(OH)\cdot CO_2H\\CH_2\cdot CO_2H\end{matrix}$$

(I.)



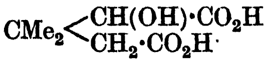
$$CH\lessdot\begin{matrix}CH_2\cdot CO_2H\\CH\cdot CO_2H\end{matrix}$$

(II.)



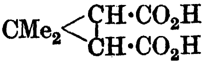
(III.)

It may be noticed in passing that the hydroxy-acid, IV, is obtained under similar conditions (*B*) from α-halogenated *gem*-dimethylglutaric acid in traces only, whilst the yield of caronic acid (V) is nearly quantitative.



$\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH(OH)\cdot CO_2H}\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}$

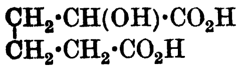
(IV.)



$\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH\cdot CO_2H}\\ |\\ \mathrm{CH\cdot CO_2H}\end{matrix}$

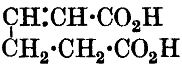
(V.)

On extending the investigation to the α-halogenated adipic acids, a marked difference in their behaviour at once became apparent, for, whilst ethyl α-chloroadipate and ethyl α-bromoadipate on boiling with a 2*N*-solution of sodium carbonate yielded more than 90 per cent. of α-hydroxyadipic acid (VI), when the same halogen compounds were heated with concentrated, methyl-alcoholic potassium hydroxide under the standard conditions used in the case of the glutaric derivatives there was obtained a mere trace of the expected *cyclo*butanedicarboxylic acid (VIII), by far the greater portion of the identified material consisting of the hydroxylation product. As in the case of α-bromoglutaric ester, so in this instance also there was obtained a small amount of the unsaturated derivative, Δ^{α}-dihydromuconic acid (VII).



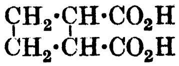
$\begin{matrix}\mathrm{CH_2\cdot CH(OH)\cdot CO_2H}\\ |\\ \mathrm{CH_2\cdot CH_2\cdot CO_2H}\end{matrix}$

(VI.)



$\begin{matrix}\mathrm{CH{:}CH\cdot CO_2H}\\ |\\ \mathrm{CH_2\cdot CH_2\cdot CO_2H}\end{matrix}$

(VII.)



$\begin{matrix}\mathrm{CH_2\cdot CH\cdot CO_2H}\\ |\quad\ \ |\\ \mathrm{CH_2\cdot CH\cdot CO_2H}\end{matrix}$

(VIII.)

Owing to the difficulties of the separation it was not found possible to account for the whole of the material as pure isolated products; the quantities actually isolated and weighed in the pure condition were as follows :

	From the chloro-ester. Per cent.	From the bromo-ester. Per cent.
α-Hydroxyadipic acid	59·0	61·0
Δ^{α}-Dihydromuconic acid	7·2	6·4
*cis-cyclo*Butane-1 : 2-dicarboxylic acid	0·9	1·3
Total isolated	67·1	68·7

It will be observed that there is scarcely any difference between the results obtained with the chloro- and the bromo-esters.

These figures indicate in a remarkably clear manner the great difficulty with which the formation of a *cyclo*butane ring is attended, as compared with a *cyclo*propane ring when similar methods of ring closure are used in the two cases.

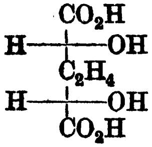
The extension of the research to αδ-dihalogenated adipic acids appeared to afford a valuable opportunity of investigating the effect on the nature of the products of stereochemical differences in the halogen compounds employed. It is not possible to examine this point in the case of ethyl αγ-dibromoglutarate, as this is obtained as a liquid mixture of *meso-* and *racemic* isomerides and cannot be satisfactorily separated into its constituents. The *meso-* and *racemic* esters of αδ-dibromoadipic acid, on the other hand, are solid substances and are easily obtained in the pure condition.

The dibromination of adipic acid has been investigated by Willstätter and Lessing (*Ber.*, 1902, **35**, 2066), who, on pouring the bromination product, prepared by the Hell-Volhard method, into ethyl alcohol, obtained an oily mixture of bromo-esters, from which one of m. p. 66° crystallised. They were unable to purify the residual oil, but on distilling it they obtained a distillate which deposited crystals of the same solid ester. The same bromination has also been described by Le Sueur (T., 1908, **93**, 718), whose observations regarding the oily portion of the product (T., 1909, **95**, 275) agree closely with those of Willstätter and Lessing. The use of thionyl chloride in place of phosphorus pentachloride for the preparation of adipyl chloride was first suggested by Stephen and Weismann (T., 1913, **103**, 269).

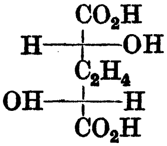
There can be no doubt but that the bromo-ester, m. p. 66°, is the *meso*-compound, for on hydrolysis with sulphuric acid (p. 962) it yielded solely the dibromo-acid, m. p. 193°, which has been described by Rosenlew (*Ber.*, 1904, **37**, 2091) and has been shown by Le Sueur and Haas to possess the *meso*-formula.

Investigation of the oily dibromination product soon made it clear that this consisted principally, although not entirely, of the *racemic* dibromo-ester. This substance, when pure, melts at 9·5° and can easily be separated by crystallisation under suitable conditions (p. 962).

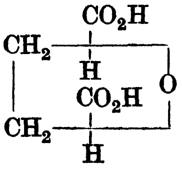
In order to leave no doubt as to the constitution of the more fusible ester, it was hydrolysed by means of sulphuric acid. Two dibromo-acids were produced, one, m. p. 193°, identical with that obtained from the less fusible ester, the other, m. p. 139°, identical, in all probability, with the isomeride of the same melting point prepared by Rosenlew (*loc. cit.*). Evidently, therefore, during the hydrolysis a partial change of configuration must have taken place with the formation of a certain quantity of *meso*-acid. That the acid, m. p. 139°, and the ester, m. p. 9·5°, have the *racemic* constitution was conclusively proved by heating them with a dilute alcoholic solution of potassium hydroxide, when, along with small quantities of the *meso-* and *racemic* dihydroxyadipic acids (IX and X), a considerable amount of *trans*-tetrahydrofurandicarboxylic acid (XII) was produced. It is clear that, whilst *cis*-tetrahydrofurandicarboxylic acid (XI) is the direct product of hydrolysis of the *meso*-acid, the *trans*-modification can only be derived without change of configuration from the *racemic* acid.



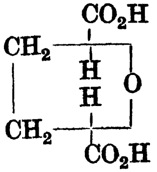
meso, m. p. 174°.
(IX.)



racemic, m. p. 146°.
(X.)



cis, m. p. 125°.
(XI.)



trans, m. p. 95°.
(XII.)

On keeping at room temperature, the *racemic* dibromo-ester changes slowly into the *meso*-form, and the melting point, originally 9·5°, becomes depressed to the extent of 2—4° every week. After several months, crystals of the *meso*-ester begin to be deposited. When the pure *racemic* ester is distilled under diminished pressure, it is converted to the extent of about 30 per cent. into the *meso*-form.

The oily dibromination product did not consist solely of the *racemic* dibromo-ester, but contained in addition the *meso*-isomeride and a third dibromo-ester which boiled at a constant temperature but could not be completely purified by distillation. The nature of this liquid ester was, however, revealed by its behaviour on hydrolysis with mineral acids, the principal product being α-keto-adipic acid, which was identified by hydrolysing its oxime to α-cyano-butyric acid and thence to glutaric acid. There can be no doubt, therefore, that the liquid dibromo-ester consisted essentially of ethyl αα-dibromoadipate :

$$CO_2Et{\cdot}CBr_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et \longrightarrow$$
$$CO_2H{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow$$
$$CO_2H{\cdot}C(\colon NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow CN{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$
$$\longrightarrow CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

In view of the property possessed by *racemic* ethyl αδ-dibromo-adipate of passing into the *meso*-isomeride, the corresponding iodo-esters were prepared in the hope that these would exhibit a smaller tendency to isomeric change.

Two iodo-esters, m. p. 92° and 46° respectively, were produced in approximately equal amounts when either of the αδ-dibromo-esters was treated with a boiling alcoholic suspension of sodium iodide. The ester, m. p. 92°, on hydrolysis with sulphuric acid, yielded a di-iodo-acid, m. p. 213°, whilst the ester, m. p. 46°, when similarly treated, gave the same di-iodo-acid together with an isomeric acid, m. p. 170°.

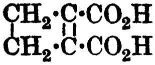
The ester, m. p. 92°, and the acid, m. p. 213°, undoubtedly possess the *meso*-configuration, for on hydrolysis with a dilute alcoholic solution of potassium hydroxide both yielded *cis*-tetrahydrofurandicarboxylic acid (XI). The ester, m. p. 46°, and the acid, m. p. 170°, when treated in the same way, gave as the main product *trans*-tetrahydrofurandicarboxylic acid (XII), and must therefore have the *racemic* configuration.

It was found, as anticipated, that the *racemic* iodo-ester, m. p. 46°, was much less easily converted into the *meso*-isomeride than the corresponding *racemic* bromo-ester.

The *meso*- and *racemic* dibromo- and di-iodo-esters, when boiled with 2*N*-sodium carbonate, yielded principally the corresponding dihydroxyadipic acids (IX and X), but on treatment with a concentrated methyl-alcoholic solution of potassium hydroxide gave a mixture of acids, of which muconic acid (XIII) was invariably the principal constituent. Besides the two hydroxyadipic acids (IX and X), the two ether-acids (XI and XII), and muconic acid, there was also isolated in two instances a sixth acid, which was ultimately identified as Δ^1-*cyclo*butene-1 : 2-dicarboxylic acid (XIV).

$CO_2H{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$

(XIII.)



$$\begin{array}{l} CH_2{\cdot}C{\cdot}CO_2H \\ \vert \quad\;\; \Vert \\ CH_2{\cdot}C{\cdot}CO_2H \end{array}$$

(XIV.)

The proportions in which these six acids were obtained from the two dibromo- and the two di-iodo-esters are shown in the following table, in which the figures representing the yields are calculated as percentages of the theoretical, and are derived from the weights of pure, separated products. It will be noticed that it was not found possible to account for quite the whole of the material, owing to the difficulties of the separation.

	Halogen derivatives used.			
	Dibromo-esters.		Di-iodo-esters.	
	Meso-.	Racemic.	Meso-.	Racemic.
	Per cent.	Per cent.	Per cent.	Per cent.
meso-Dihydroxyadipic acid	16	5	23	2
racemic Dihydroxyadipic acid	9	7	14	3
cis-Tetrahydrofurandicarboxylic acid	13	7	23	2
trans-Tetrahydrofurandicarboxylic acid	0	10	0	4
Muconic acid	55	60	33	78
*cyclo*Butene-1 : 2-dicarboxylic acid	0	2	0	4
Total isolated	93	91	93	93

The main point of interest arising from these figures is the extremely small amount of the *cyclo*butenedicarboxylic acid formed. This result is the more striking when it is remembered that in the corresponding experiment with ethyl dibromoglutarate nearly

90 per cent. of the material became involved in ring formation. This contrast is clearly in agreement with the indications of the hypothesis outlined on p. 953.

Another noteworthy feature of the results is the high yield of muconic acid which was obtained. It happens that muconic acid, although a substance of very great interest, is a difficult material to prepare in quantity. It was obtained by Rupe (*Annalen*, 1890, **256**, 1) and by Ruhemann and Blackmann (T., 1890, **57**, 370) from mucic acid, which was converted successively into dichloromuconic acid (Bode, *Annalen*, 1864, **132**, 95), dihydromuconic acid, βγ-dibromoadipic acid (Ador, *Ber.*, 1871, **4**, 627; Limpricht, *Annalen*, 1872, **165**, 262), and finally into muconic acid:

$$\begin{gathered}CO_2H{\cdot}[CH{\cdot}OH]_4{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH{:}CCl{\cdot}CCl{:}CH{\cdot}CO_2H \longrightarrow \\ CO_2H{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H \longrightarrow \\ CO_2H{\cdot}CH_2{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2H \longrightarrow \\ CO_2H{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H.\end{gathered}$$

This rather lengthy process has the disadvantage of a poor yield in the initial reaction. A much more direct synthesis, devised by Döbner (*Ber.*, 1902, **35**, 1147), consists in heating glyoxal with malonic acid,

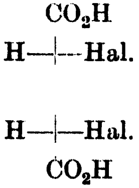
$$\begin{gathered}CHO{\cdot}CHO+2CH_2(CO_2H)_2 \longrightarrow CO_2H{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H+ \\ 2H_2O+2CO_2,\end{gathered}$$

but the yield is only 2 per cent. of the theoretical, and, although Behrend and Koolman (*Annalen*, 1912, **394**, 228) have effected a considerable improvement by replacing glyoxal by its bisulphite compound, large quantities of succinnic acid and syrupy matter are formed and the yield of muconic acid rarely reaches more than 10 per cent., calculated on the glyoxal employed. Attempts have also been made by Le Sueur (T., 1909, **95**, 273; see also Le Sueur and Haas, T., 1910, **97**, 173) and by Stephen and Weismann (*loc. cit.*) to prepare muconic acid directly from the dibromination product of adipic acid, but only with a limited degree of success; in fact, Le Sueur and Haas were considerably impressed with the smallness of the quantity of muconic acid produced, and regarded it as due to the existence of a strong tendency towards the production of a five-membered heterocyclic ring, the formation of which necessarily limited the quantity of the unsaturated acid produced simultaneously. It would appear, however, from the results tabulated, that this inference requires modification, and that the extent to which the unsaturated acid is formed is merely a question of experimental conditions. By observing the correct conditions (p. 967) it is possible to prepare muconic acid easily and in large quantities from commercial *cyclo*hexanol (pp. 961 and 962).

The contrast between the large yield of muconic acid obtained from αδ-dibromoadipic esters and the small quantity of dihydromuconic acid produced under similar conditions from the α-monobromo-derivative is probably to be attributed to the strong tendency, of which numerous examples are to be found in chemical literature, towards the formation of conjugated unsaturated systems.

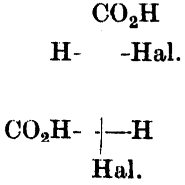
As regards the other products isolated from the esters of the dihalogenated acids, a reference to the table on p. 957 shows that the evidence obtained by comparing the behaviour of the stereoisomeric halogen compounds is distinctly in favour of the view that the relative rotation of the two asymmetric groups in the dihalogenadipic esters is limited by a considerable tendency towards the formation of special configurations. It will be recalled that such substances as αβ-dimethylsuccinnic acid (Bone and Perkin, T., 1896, **69**, 266) and αγ-dimethylglutaric acid (Auwers and Thorpe, *Annalen*, 1895, **285**, 310) exist in *meso-* and *racemic* modifications, one of which passes into an anhydride much more readily than the other. Evidently, therefore, the free rotation of the different parts of the molecule around the bonds uniting the carbon atoms must be limited by the tendency of the molecule as a whole to assume certain particular configurations, which, in the instances cited, are different for the two stereoisomerides. No evidence has hitherto been recorded of a similar phenomenon amongst derivatives of adipic acid, and, as on general grounds there must be some connexion between the tendency opposing rotation and the number of carbon atoms in the chain joining the asymmetric groupings, it is of interest to observe that derivatives of adipic acid containing equivalent asymmetric carbon atoms in the two α-positions fall into line with those of succinnic acid and glutaric acid in this respect.

The esters of the *meso*-dihalogenated acids, for example, might have a favoured configuration corresponding more or less closely with one of the following types:



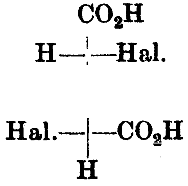
$$\begin{array}{c} \mathrm{CO_2H} \\ \mathrm{H—|—Hal.} \\ \\ \mathrm{H—|—Hal.} \\ \mathrm{CO_2H} \end{array}$$

(*meso-α*).



$$\begin{array}{c} \mathrm{CO_2H} \\ \mathrm{H-\quad -Hal.} \\ \\ \mathrm{CO_2H-|—H} \\ \mathrm{Hal.} \end{array}$$

(*meso-β*).

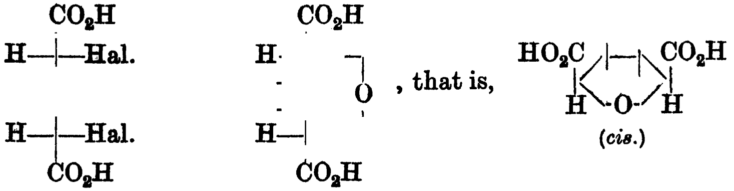


$$\begin{array}{c} \mathrm{CO_2H} \\ \mathrm{H—|—Hal.} \\ \\ \mathrm{Hal.—|—CO_2H} \\ \mathrm{H} \end{array}$$

(*meso-γ*).

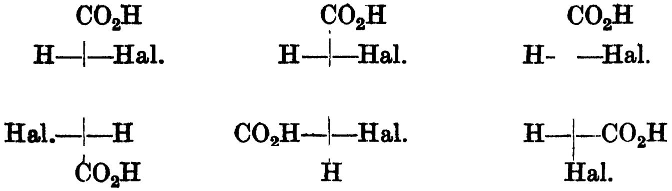
However, the fact that both the *meso*-bromo- and *meso*-iodo-esters yield only the *cis*-modification of tetrahydrofurandicarboxylic acid

(XI, p. 956) clearly indicates the *meso-α* configuration to be the stable one.



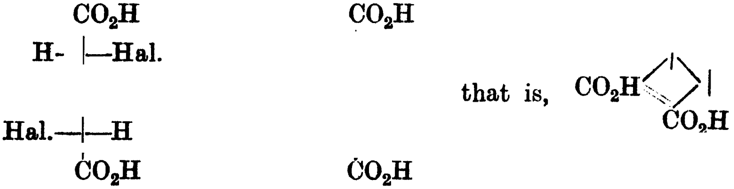
(*cis.*)

Similarly, the configuration of the *racemic* esters, which might approximate to either of the following:

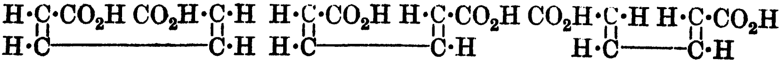


(*racemic-α*). (*racemic-β*). (*racemic-γ*).

is indicated, first by the fact that each of these esters, particularly the more stable iodo-ester, yields only a small amount of *trans*-tetrahydrofurandicarboxylic acid (which ought readily to be formed from an ester of the racemic-β type), and a yet smaller quantity of the *cis*-isomeride, and, secondly, by the fact that from the *racemic* esters alone is it possible to obtain the *cyclo*butenedicarboxylic acid. The *racemic-α* configuration, therefore, appears to be the favoured one:



The large yield of muconic acid from the *racemic* esters and particularly from the less easily isomerised *racemic* iodo-ester is also in agreement with these deductions. Muconic acid, according to current stereochemical views, should exist in three forms, which may be designated the *cis*-, *amphi*-, and *trans*-forms respectively.



(*cis*). (*amphi*). (*trans*).

In the experiments herein recorded, only one muconic acid (m. p. 305°) has been met with, and this is undoubtedly identical (see

p. 967) with the acid which has previously been obtained by other workers (p. 958) and has been shown by Behrend and Heyer (*Annalen*, 1919, **416**, 294) to possess the *trans*-configuration. Now an examination of the projection formulæ shows that, whilst either the α-, β-, or γ-form of the esters of the *meso*-dihalogenated acids, and the β- and γ-forms of the *racemic* esters could yield any one of the three theoretically possible modifications of muconic acid, the *racemic*-α-esters should give rise to the *trans*-form only. It would therefore appear that the formation of muconic acid from the *meso*-esters is dependent on a preliminary change to the *racemic* configuration.

EXPERIMENTAL.

(A) *Preparation of Adipic Acid.*

The adipic acid used in these experiments was prepared by oxidising commercial *cyclo*hexanol with nitric acid by the method recommended by Bouveault and Locquin (*Bull. Soc. chim.*, 1908, **146**, 432), which is very easily carried out with considerable amounts of material.

(B) *Monohalogenation of Adipic Acid.*

A mixture of adipic acid (500 grams) and thionyl chloride (1000 grams) was warmed until no more sulphur dioxide was evolved. Iodine (10 grams) was then added and a rapid stream of chlorine passed into the mixture at 80° until the theoretical increase in weight was obtained.

Ethyl α-Chloroadipate.

The ester was prepared by pouring the crude chlorination product into ethyl alcohol, and was collected in ether after adding water. Traces of acidic products were removed by sodium carbonate, the extract was washed and dried, and the oil remaining after evaporation of the ether repeatedly distilled until the monochloro-ester boiled at 129—131°/10 mm. (Found: Cl=14·9. $C_{10}H_{17}O_4Cl$ requires Cl=15·0 per cent.).

Ethyl α-Bromoadipate.

This ester was prepared similarly to the chloro-compound and was isolated in the same way. It was considerably more difficult to purify by distillation than the chloro-compound, but was ultimately obtained as a liquid, b. p. 161—163°/11 mm. (Found: Br=28·8. $C_{10}H_{17}O_4Br$ requires Br=28·5 per cent.).

(C) *Dihalogenation of Adipic Acid.*

The dibromination of adipic acid was carried out similarly to the monobromination, 500 grams of adipic acid, 1000 grams of thionyl chloride, and 1250 grams of bromine being used. The process can be completed in four to eight hours (according to the intensity of the light) and there is no necessity to heat for forty hours, as suggested by Stephen and Weismann (*loc. cit.*). The ethyl esters were prepared by pouring the crude bromination product into ethyl alcohol, and isolated as in the case of the monohalogenated esters.

Ethyl meso-*αδ-Dibromoadipate.*

The mixture of isomeric dibromo-esters, b. p. 191—194°/16—17 mm., obtained in a yield of 93 per cent. of the theoretical, set, after forty-eight hours, to a paste consisting of about equal weights of oil and crystals. The latter, when drained and recrystallised from ethyl alcohol, yielded the pure *meso*-dibromo-ester (Found: Br=44·3. Calc., Br=44·4 per cent.).

When the bromo-ester was dissolved in cold, concentrated sulphuric acid, a small quantity of water added, and the mixture boiled, hydrolysis occurred and *meso*-dibromoadipic acid was obtained (Found: Br=52·5. Calc., Br=52·6 per cent.).

Ethyl r-*αδ-Dibromoadipate.*

The oil drained from the *meso*-ester was dissolved in ethyl alcohol and the solution cooled to −30°. The crystals which separated were washed with alcohol at −30° and dried at the same temperature over sulphuric acid in a vacuum.

When freshly prepared, the racemic ester melts at 9·5° and can be kept for several weeks at 0° without change. The effect of keeping it at room temperature and of distillation has been noted on p. 956 (Found: Br=44·6. $C_{10}H_{16}O_4Br_2$ requires Br=44·4 per cent.).

When the ester is hydrolysed by moderately concentrated sulphuric acid, a considerable quantity of r-αδ-dibromoadipic acid is obtained (Found: Br=52·45. Calc., Br=52·6 per cent.), along with a small amount of the *meso*-isomeride.

The constitutions of these racemic compounds were proved by converting them by means of 2*N*-ethyl-alcoholic potassium hydroxide into *trans*-tetrahydrofuran-2:5-dicarboxylic acid, a substance which has previously been prepared and characterised by Lean (T., 1900, **77**, 115). The method of isolation and purification of the tetrahydrofurandicarboxylic acid was similar to that described on pp. 967, 968.

Ethyl αα-Dibromoadipate.

The alcoholic filtrate from the first crystallisation of the *racemic* dibromo-ester was evaporated and the residue cooled to 0°. The crystals of the *meso*-ester which separated were drained, and the oil was again crystallised from alcohol at −30°. The residual oil was then distilled (b. p. 190—193°/10 mm.) and the alternate crystallisation of the stereoisomerides repeated twice in each case. After another distillation, four alternate crystallisations of the *meso*- and *racemic* esters, and a final distillation, no more crystals could be obtained by any of the above methods. That the liquid ester, b. p. 192—193°/10·5 mm. (Found: Br=44·5. $C_{10}H_{16}O_4Br_2$ requires Br=44·4 per cent.), consists essentially of ethyl αα-dibromoadipate is proved by the fact that α-ketoadipic acid is the principal product of hydrolysis.

The hydrolysis was effected by dilute ethyl-alcoholic potassium hydroxide solution, and the potassium salts were collected and dissolved in dilute hydrochloric acid. The acid was extracted with ether, and, after crystallising from this solvent, melted at 124° (compare Gault, *Compt. rend.*, 1909, **148**, 1113). It was identified by analysis (Found: C=44·9; H=5·0. Calc., C=45·0; H=5·0 per cent.), and by conversion into its oxime, m. p. 152°, which, when hydrolysed successively with boiling water and alkali, yielded glutaric acid identical with that obtained from *cyclo*pentanone by oxidation.

Ethyl meso-*αδ-Di-iodoadipate.*

This ester forms about 50 per cent. of the product obtained when either the *meso*- or the *racemic* αδ-dibromo-ester is boiled with an alcoholic suspension of sodium iodide. It is most convenient, therefore, to use for this preparation the mixture of isomerides obtained by distilling the oil produced by the action of ethyl alcohol on the crude dibromination product.

The distilled oil (1000 grams) was boiled for one hour in an iron vessel with 95 per cent. alcohol (1500 c.c.) and finely divided sodium iodide (1000 grams), and the product, after cooling, poured into water (15 litres), which was vigorously stirred until the precipitated iodo-esters had congealed to a dough-like mass. This was kneaded under fresh water to remove adhering salts and the product crystallised from 2·5 litres of 95 per cent. alcohol. The *meso*-iodo-ester separated in dense needles, m. p. 88—90°; when recrystallised for analysis, it melted at 92° (Found: I=56·3. $C_{10}H_{16}O_4I_2$ requires I=56·0 per cent.).

meso-αδ-*Di-iodoadipic Acid.*

This acid was obtained by hydrolysing the ester (m. p. 92°) by means of moderately concentrated sulphuric acid. The product crystallised from glacial acetic acid in minute needles melting and decomposing at 213° (Found: I=63·4. $C_6H_8O_4I_2$ requires I=63·8 per cent.).

In order to prove the constitution of this acid, it was converted by boiling with 2*N*-ethyl-alcoholic potassium hydroxide into *cis*-tetrahydrofuran-2:5-dicarboxylic acid (compare Lean, *loc. cit.*), the method of isolation and purification being similar to that described on pp. 967, 968. The ester, m. p. 92°, was treated in the same way with similar results.

Ethyl r-αδ-*Di-iodoadipate.*

On pouring into water the alcoholic solution from which the *meso*-isomeride had crystallised (p. 963), a solid product was formed, which, when dried and crystallised several times from light petroleum, separated in clusters of fine needles, m. p. 46° (Found: I=55·8. $C_{10}H_{16}O_4I_2$ requires I=56·0 per cent.).

r-αδ-*Di-iodoadipic Acid.*

This acid was prepared from its ester as in the case of the *meso*-isomeride. In the present instance, however, a considerable separation of iodine and gummy matter occurred, and it was necessary to purify the product by rubbing with chloroform and crystallising from formic acid. In this way r-αδ-*di-iodoadipic acid*, m. p. 170° (decomp.), was obtained (Found: I=63·7. $C_6H_8O_4I_2$ requires I=63·8 per cent.), along with a small quantity of the *meso*-isomeride.

The constitution of the acid, m. p. 170°, was proved by hydrolysing it with dilute, alcoholic potassium hydroxide solution to *trans*-tetrahydrofuran-2:5-dicarboxylic acid, the experiment being carried out as in the case of the *racemic* dibromo-acid. The *racemic* di-iodo-ester, m. p. 46°, when treated in the same way, gave similar results.

(D) *Action of Dilute Alkalis on the Esters of Monohalogenated Adipic Acid. Formation of α-Hydroxyadipic Acid.*

The esters of monochloro- and monobromo-adipic acids were boiled with 2*N*-sodium carbonate under the conditions employed in the case of the monohalogen derivative of glutaric acid (this vol.,

p. 318). In the present instances α-hydroxyadipic acid (compare Ince, T., 1895, **67**, 159; also p. 966 below) appeared to be the sole product.

(E) *Action of Concentrated Alkalis on the Esters of Monohalogenated Adipic Acid. Formation of α-Hydroxyadipic Acid, Δ^{α}-Dihydromuconic Acid, and* cis-cyclo*Butane*-1 : 2-*dicarboxylic Acid.*

Ethyl α-chloroadipate (180 grams) or ethyl α-bromoadipate (211 grams) was allowed to flow in a thin stream into a boiling 6*N*-solution (1 litre) of dry potassium hydroxide in pure methyl alcohol. After being heated for a short time, the mixture was diluted with ethyl alcohol (2 litres) and filtered, the residue on the filter being washed with 90 per cent. ethyl alcohol until only inorganic salts remained.

The original alkaline filtrate was treated with excess of carbon dioxide, and, after the carbonates had been removed, was evaporated, the residue being worked up for acid products with the aid of acetone as solvent. The syrupy acids were then dissolved in a slight excess of 2·5*N*-ethyl-alcoholic potassium hydroxide, and the insoluble potassium salt collected.

The 90 per cent. ethyl-alcoholic washings were evaporated with the addition of benzene and the precipitate which separated was collected and washed with ethyl alcohol.

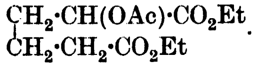
Δ^{α}-*Dihydromuconic Acid* (VII).

The insoluble potassium salts were dissolved in dilute hydrochloric acid. The Δ^{α}-dihydromuconic acid which crystallised was identified by its melting point (169°), by analysis (Found : C=49·7; H=5·7. Calc., C=50·0; H=5·6 per cent.), by conversion into its methyl ester (m. p. 86°; Rupe, *loc. cit.*), and by direct comparison with a specimen prepared from muconic acid.

cis-cyclo*Butane*-1 : 2-*dicarboxylic Acid* (VIII).

The alcoholic filtrates from the potassium salt of the unsaturated acid were evaporated and the residues worked up for the acid products, acetone being the solvent employed. The syrupy acids were then digested with acetyl chloride and the residue, after evaporation of the acetic acid and excess of acetyl chloride, was distilled at 140°/25 mm. in a current of nitrogen, a well-cooled scrubbing column being used as receiver. The distillate was boiled with water and the turbid liquid, after being poured through a wet filter, was evaporated. The crystalline residue was drained on porous tile and recrystallised from a small amount of water, when well-defined, prismatic needles, m. p. 136—137°, separated. The acid did not decolorise cold alkaline permanganate and was identified with Perkin's *cis-cyclo*butane-1:2-dicarboxylic acid (T., 1894, **65**, 582) by analysis (Found: C=50·25; H=5·7. Calc., C=50·0; H=5·6 per cent.), and by conversion into the anil (Found: N=6·91. Calc., N=6·95 per cent.), which melted at 127°, the temperature recorded by Perkin.

Ethyl α-Acetoxyadipate,



$$\begin{array}{l} CH_2{\cdot}CH(OAc){\cdot}CO_2Et \\ | \\ CH_2{\cdot}CH_2{\cdot}CO_2Et \end{array}.$$

The residue from the distillation of the *cyclo*butanedicarboxylic anhydride was esterified with ethyl alcohol by the zinc chloride-benzene method, and the ester digested with a further quantity of acetyl chloride. The product, b. p. 146—150°/6—7 mm. (Found: C=55·5; H=7·7. $C_{12}H_{20}O_6$ requires C=55·4; H=7·7 per cent.), yielded α-hydroxyadipic acid on hydrolysis.

α-Hydroxyadipic Acid (VI).

The above ester was boiled for twelve hours with concentrated hydrochloric acid. Crystals of the acid separated on evaporation, and were recrystallised from ethyl acetate (Found: C=44·6; H=6·3. Calc., C=44·4; H=6·1 per cent.). M. p. 152° (compare Ince, *loc. cit.*).

(F) *Action of Dilute Alkalis on the Esters of αδ-Dihalogenated Adipic Acid. Formation of* meso- *and* racemic *αδ-Dihydroxyadipic Acids.*

The *meso-* and *racemic* modifications of ethyl αδ-dibromoadipate and αδ-di-iodoadipate, on boiling with 2*N*-sodium carbonate solution under the standard conditions employed in the case of the glutaric acid derivatives (this vol., p. 322), yielded solely the corresponding αδ-dihydroxyadipic acids dealt with on p. 970.

(G) *Action of Concentrated Alkalis on the Esters of αδ-Dihalogenated Adipic Acid. Formation of* meso- *and* racemic *αδ-Dihydroxyadipic Acids,* cis- *and* trans-*Tetrahydrofuran-2:5-dicarboxylic Acids, Muconic Acid, and* Δ^1-cyclo*Butene-1:2-dicarboxylic Acid.*

The ester (360 grams of the *meso-* or *racemic* dibromo-ester, or 454 grams of either di-iodo-ester) was heated to 100° and poured in a thin stream into a boiling 6*N*-solution (1800 c.c.) of dry potassium hydroxide in pure methyl alcohol, the experimental conditions being similar to those employed in the case of dibromoglutaric ester.

Muconic Acid (XIII).

The insoluble potassium salts, which consisted almost exclusively of potassium muconate and potassium bromide, were collected, thoroughly washed with methyl alcohol, then dried, and mixed with an excess of dilute hydrochloric acid. After some hours, the precipitated muconic acid was collected and washed with water. It was identified by analysis (Found: C=50·8; H=4·4. Calc., C=50·7; H=4·2 per cent.), by its high m. p. (301—305°) and remarkable insolubility, and by the m. p. of its methyl and ethyl esters (154° and 62° respectively).

In preparing muconic acid for further research by this method, it is sufficient to use the crude oil obtained by the action of ethyl alcohol on the dibromination product of adipic acid, as distillation or crystallisation of the separate isomerides does not improve the ultimate yield of muconic acid, which, even from the crude mixture of esters, amounts to 50 per cent. of the weight of adipic acid employed.

The aqueous solution from which the muconic acid was precipitated was found to contain, besides a trace of muconic acid, a very small amount of an acid syrup, which was added to the alcoholic solution of the potassium salts.

cis-*Tetrahydrofuran*-2 : 5-*dicarboxylic Acid* (XI).

The methyl-alcoholic solution of potassium salts was diluted with a large volume of absolute ethyl alcohol, and the potassium salt which gradually separated was collected by filtration.

The filtrates were evaporated and the residue worked up for acid products with the aid of acetone as solvent. The gummy mixture of acids was then quantitatively esterified with ethyl alcohol by the benzene method, and the esters were separated by distillation through a short fractionating column into four fractions: (*a*) b. p. 145—150°/10 mm., (*b*) b. p. 150—158°/10 mm., (*c*) b. p. 158—166°/10 mm., and (*d*) b. p. 166—174°/10 mm. Each fraction was now boiled for four hours with 1·2 times its weight of potassium hydroxide in 1·2*N*-ethyl-alcoholic solution. The product from fraction (*a*) usually deposited crystals, but not the others. Ether was now added to the four products of hydrolysis in quantities proportional to the weights of the original fractions and the addition repeated daily until the product from fraction (*d*) commenced to crystallise. The potassium salts were then collected, and, along with the salt which separated from the mixture of methyl and ethyl alcohols, worked up for acid products.

When either of the *meso*-halogen esters was used, there was generally no difficulty in obtaining these acid products in the solid condition, the principal constituent being *cis*-tetrahydrofuran-2:5-dicarboxylic acid, which was purified by crystallisation from a mixture of ethyl acetate and light petroleum in prisms, m. p. 124—125° (Found: C=45·0; H=5·1. M=159. Calc., C=45·0; H=5·0 per cent. M=160) (compare Lean, T., 1900, **77**, 110; Le Sueur, T., 1908, **93**, 716).

The residues from the crystallisation of the tetrahydrofurandicarboxylic acid yielded a solid substance, m. p. 110—137°, which as it dissolved in moderately concentrated, ethyl-alcoholic potassium hydroxide solution without the formation of a precipitate, was added to the combined alcoholic filtrates from which the potassium salt of the tetrahydrofurandicarboxylic acid had been obtained.

Δ^1-cyclo*Butene-1:2-dicarboxylic Acid* (XIV).

When either of the esters of the *racemic* dihalogenated acids was used for these experiments, the products obtained in place of *cis*-tetrahydrofuran-2:5-dicarboxylic acid consisted of straw-coloured syrups, which resisted every effort to separate them into their constituents until it was discovered that crystals could be obtained from products of esterification with methyl alcohol.

The methyl esters were prepared by the action of methyl iodide on the silver salts, and crystallisation, having been started, was allowed to proceed in ethyl-alcoholic solution at −30° to −35°. The solid ester was purified by crystallisation from light petroleum. It melted at 44—45° and was identified as the methyl ester of Δ^1-*cyclo*butene-1:2-dicarboxylic acid by analysis (Found: C=56·3; H=6·0. Calc., C=56·5; H=5·9 per cent.), by the formation of a crystalline dibromide, m. p. 84 (Found: Br=48·7. Calc., Br=48·5 per cent.), and by hydrolysis to the corresponding unsaturated acid, which, after crystallising from water, melted at 177°, and closely agreed in its properties with the acid described by Perkin (*loc. cit.*) (Found: C=50·9; H=4·35. Calc., C=50·7; H=4·2 per cent.).

trans-*Tetrahydrofuran-2:5-dicarboxylic Acid* (XII).

The methyl-alcoholic filtrate from which the unsaturated ester had crystallised was evaporated, and the oily residue was dissolved in chloroform. Bromine was added until the colour was permanent, and the product, after the solvent had been evaporated, was distilled. The distillate, b. p. 127—131°/10 mm., was then hydrolysed by means of 2*N*-ethyl-alcoholic potassium hydroxide solution, and, after evaporation of the alcohols, the acid product was isolated in the usual manner, acetone being the solvent employed. The syrup obtained consisted mainly of the *cis*- and *trans*-forms of the tetrahydrofurandicarboxylic acid, and from it the *cis*-acid was caused to crystallise as completely as possible in the presence, first of ethyl acetate, and finally of a mixture of this with light petroleum. The final residues, on mixing with concentrated hydrochloric acid, quickly set to a thick paste of crystals of the *trans*-acid, which was collected on porous tile and dried over phosphoric oxide in a vacuum. The acid melted at 94—95° (Found: C=44·95; H=5·35. Calc., C=45·0; H=5·0 per cent.), and its hydrate at 63—65°, as recorded by Lean (*loc. cit.*).

The acids contained in the liquid taken up by the porous tile were found to be soluble without the separation of a precipitate in ethyl-alcoholic potassium hydroxide solution, and were therefore added to the ethyl-alcoholic solution from which the original potassium tetrahydrofurandicarboxylates were obtained.

A separation of *cis*- and *trans*-tetrahydrofuran-2 : 5-dicarboxylic acids may also be effected by fractional esterification with ethyl alcohol in the presence of zinc chloride, the first portion of the material to become insoluble in water consisting principally of the *trans*-ester.

Another method of separation consists in fractionally hydrolysing the mixed esters. When ethyl-alcoholic potassium hydroxide solution is used, the first crop of crystals which separates consists almost entirely of the potassium salt of the *trans*-acid. However, it was found to be difficult to purify the *cis*-acid by this method owing to the slight solubility of its potassium salt in alcohol.

meso-$\alpha\delta$-*Dihydroxyadipic Acid* (IX).

The combined ethyl-alcoholic filtrates from the potassium salts of the tetrahydrofurandicarboxylic acids were evaporated to dryness, and the residue worked up for organic acids with the aid of acetone as solvent. The solid product was crystallised from acetone, and the less soluble fraction thus obtained again crystallised from water, from which it separated in small prisms, m. p. 174° (Found: C=40·3; H=5·7. Calc., C=40·4; H=5·6 per cent. Found: for the silver salt, Ag=55·0. Calc., Ag=55·1 per cent.) (compare Rosenlew, *loc. cit.*).

r-$\alpha\delta$-*Dihydroxyadipic Acid* (X).

The more soluble residues from the crystallisation of the *meso*-acid were purified by crystallisation from ethyl acetate until the m. p. remained constant at 146° (Found: C=40·2; H=5·6. Calc., C=40·4; H=5·6 per cent. Found: for the silver salt, Ag=54·9. Calc., Ag=55·1 per cent.) (compare Rosenlew, *loc. cit.*).

The ultimate residue obtained after crystallising the two isomeric dihydroxyadipic acids was syrupy in character, but on treatment with appropriate solvents (pp. 968, 969) yielded small amounts of both the *cis*- and *trans*-forms of tetrahydrofuran-2:5-dicarboxylic acid (*q.v.*).

In conclusion, I desire to express my indebtedness for the valuable criticisms and suggestions which I have received on many occasions at Professor Thorpe's research meetings from various members of this College.

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CVI.—*The Velocity of Reaction in Mixed Solvents. Part I. The Velocity of Saponification of Two Ethyl Esters in Ethyl Alcohol-Water Mixtures.*

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THE velocity with which the same reaction takes place in a series of widely differing solvents has been measured in numerous cases, but only a very limited number of reactions have been investigated in solvent media containing varying proportions of two constituents.

If a curve be drawn showing the relation between the velocity constant k and the composition of a binary solvent medium, is it to be assumed that k is a linear function of the composition of the solvent medium? The evidence appears to be very conflicting, but in investigations covering a wide range of reactions and widely differing solvent media it would appear that a maximum or minimum or a marked change in the direction of the curve is a common feature (Herz, *Ber.*, 1907, **40**, 2898; Tubandt, *Annalen*, 1907, **354**, 259; Burrows, T., 1919, **115**, 1230; Bohnsen, *J. Physical Chem.*, 1920, **24**, 677). Nevertheless, in the case of the formation of the quaternary ammonium salts in binary solvent mixtures, the conclusion is drawn that *k* is a linear function of the composition of the solvent, provided the components have similar chemical characters (Hemptinne, *Zeitsch. physikal. Chem.*, 1899, **28**, 225).

In the majority of these investigations the number of the mixtures of the two solvents in which the reaction has been examined has been too small for any very definite conclusions to be drawn.

Ethyl alcohol and water have been used as the components of a solvent medium in numerous cases (Walker, T., 1897, **71**, 489; Bredig, *Ber.*, 1906, **39**, 1756; Goldschmidt, *Zeitsch. physikal. Chem.*, 1907, **60**, 728; Lapworth, T., 1908, **93**, 2167; Fawsitt, T., 1914, **105**, 609; Bohnsen, *loc. cit.*), and it is very noticeable that whether the action of water is to accelerate or to retard the reaction, the curve shows points of inflexion.

The velocity of esterification of benzoic and substituted benzoic acids in alcohol containing up to 10 per cent. of water has been shown to be inversely proportional to a function of the concentration of the water over this range (Kailan, *Monatsh.*, 1906, **27**, 543 *et seq.*), a result which is the reverse of that obtained in our present investigation.

A complication is introduced into the study of reactions taking place in alcohol–water mixtures when one of the reactants is capable of forming a metallic ethoxide. An equilibrium is then set up which will be expressed by the equation :

$$MOH + C_2H_5{\cdot}OH = MOC_2H_5 + H_2O,$$

consequently a reaction may proceed in such a way that simultaneously a derivative of the ethoxide and of the hydroxide will result. It is improbable that these two simultaneous reactions will proceed with the same velocity and will be equally influenced by the changing of the solvent medium. The rate of reaction between *o*-dinitrobenzene and sodium alkyloxide in alcohol–water mixtures has been determined and the proportion of the hydroxy- to the ethoxy-derivative estimated (Lobry de Bruyn, *Rec. trav. chim.*, 1899, **18**, 41). Even in alcohol–water mixtures containing a large percentage of water the proportion of ethoxy-derivative is exceptionally large; and in any one experiment this proportion remains constant. It has been deduced from this ratio that sodium divides itself between alcohol and water in proportion to the amounts of derivatives formed. This deduction does not appear satisfactory, as the equilibrium between the metallic ethoxide and hydroxide will be continuously disturbed by the simultaneous reactions taking place at different speeds, and at the same time will tend continuously to maintain itself and must be fixed, therefore, by the composition of the solvent. Reactions showing a similar complication have been investigated by Donnan (*Zeitsch. physikal. Chem.*, 1909, **69**, 159), Senter (T., 1915, **107**, 1070; 1916, **109**, 681) and Cox (T., 1920, **117**, 493).

In a previous communication, McCombie and Scarborough (T., 1915, **107**, 156) began an investigation on the velocity of saponification of ethyl benzoate in ethyl alcohol–water mixtures, the composition of the solvent being expressed as volume per cent.

The curve showing the relation between k and the composition of the solvent was found to correspond, in outline, with that obtained by Kremann (*Monatsh.*, 1905, **26**, 279), who studied the rate of saponification of ethyl acetate under similar conditions. A closer examination of our curve showed certain points of inflexion unobserved by Kremann. At this point the work was interrupted; it has now been resumed and the conditions of experiment have been considerably altered. Two esters were chosen, ethyl benzoate and ethyl *iso*butyrate, as esters of a typical aromatic and a typical aliphatic acid, and, further, the velocity constants of these esters were nearly the same.

A consideration of the results given in Table II shows that the value of k, calculated from the equation

$$k=\frac{2\cdot3}{a-b}\, t.\log\frac{a-x}{b-x}\cdot\frac{b}{a} \quad \ldots\ldots \quad \text{(i)}$$

is constant over the range of the reaction. Thus the reaction is bimolecular, and may be represented by the equation:

$$R\cdot CO_2\cdot C_2H_5+KOH=R\cdot CO_2K+C_2H_5\cdot OH.$$

From Table I it is evident that the value of k is independent of the initial concentration of the ester and of the alkali within the limits of error.

The ratio of the velocity constant for ethyl *iso*butyrate to that of ethyl benzoate is very nearly constant, and appears to have a mean value of

$$k_{\text{ethyl }iso\text{butyrate}}/k_{\text{ethyl benzoate}}=1\cdot1$$

for any one solvent mixture. It may be deduced from this that, even with two such widely differing esters as these, the chemical character of the esters does not influence the general type of the curve showing the relation between the velocity constant and the composition of the solvent medium.

In tables III and IV it is seen that the value of k is very small in 100 per cent. alcohol, and increases markedly as the percentage of the alcohol is decreased. The value of k in water is of the order of 2000 times as great as that in 100 per cent. alcohol. The velocity constant for the reaction between the ester and potassium ethoxide in 100 per cent. alcohol has been found to be very small, and about one-third (k=0·0005) of that for the reaction between potassium hydroxide and the ester in 100 per cent. alcohol. This is in agreement with the results obtained by Kremann (*loc. cit.*). It is to be presumed that this reaction may be represented by the equation:

$$R \cdot CO_2 \cdot C_2H_5 + KOC_2H_5 = (C_2H_5)_2O + R \cdot CO_2K;$$

the amount of ether formed in this reaction would be too small for detection.

From results obtained by Lobry de Bruyn (*loc. cit.*) it must be concluded that the equilibrium in 100 per cent. alcohol,

$$KOH + C_2H_5 \cdot OH \rightleftharpoons KOC_2H_5 + H_2O,$$

must proceed almost exclusively towards the right. Thus, as the concentration of the potassium hydroxide, as such, must be very low, it follows that the velocity of saponification of an ester by potassium hydroxide in absolute alcohol is not truly represented by the observed value.

A consideration of the curves seems to show that we are dealing with some process which passes through a succession of phases, in each of which the relation between the velocity constant and the composition of the medium is approximately linear. It was found that the curves could be divided into four phases, of which the first is expressed very inadequately by a linear function. The observed and calculated values for two phases are given in the appended table:

Ethyl Benzoate.

Alcohol per cent.	$k_{obs.}$	$k_{calc.}$	Alcohol per cent.	$k_{obs.}$	$k_{calc.}$
97·5	0·0165	0·0161	60	0·133	0·131
95	0·0279	0·0274	50	0·205	0·210
90	0·0487	0·0461	46	0·243	0·241
85	0·0633	0·0670	42	0·280	0·278
			40	0·290	0·289

There is a period of transition between 35 per cent. and 30 per cent. alcohol. The points of intersection of these straight lines were calculated, and the critical points were found to be 80·5, 60, and 31 per cent. alcohol; these points are common to the curves for both esters. It was noticed that these percentages corresponded very closely with simple integral ratios; it seemed possible that complexes might exist composed of the two components of the solvent in the proportions of these percentages. The value 80·5 per cent. alcohol corresponds very closely with the composition required by the complex $5C_2H_5{\cdot}OH,3H_2O$; similarly, 60 per cent. alcohol corresponds with a complex of the composition $3C_2H_5{\cdot}OH,5H_2O$, and 30 per cent. alcohol with a complex of the composition $C_2H_5{\cdot}OH,6H_2O$.

At this stage of the proceedings it seems to the authors premature to offer any explanation of these phenomena; it is their intention to extend the investigation to the esters of other fatty acids and of substituted aromatic acids in alcohol–water mixtures and in other pairs of solvents. Certain reactions other than the saponification of esters are being studied.

EXPERIMENTAL.

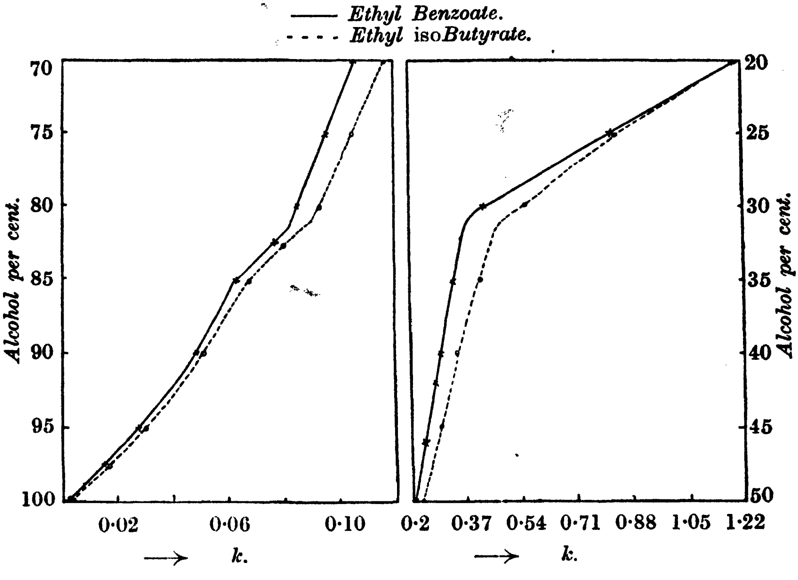
The ethyl alcohol was obtained from rectified spirit and purified by distillation with lime and a subsequent, prolonged boiling with sodium hydroxide. It was then fractionated carefully, and, by means of a pyknometer, its density, determined at 15°, compared with that of water at 4°. In order to prepare an alcohol–water mixture of a definite composition, a weighed quantity of this alcohol was mixed with the calculated weight of water, and its density again determined. The mixture was adjusted, if necessary, with either alcohol or water until the composition was within 0·05 per cent. of that required. Two determinations of the density of the final mixture were made. The alcohol–water mixtures were stored in sealed bottles, and the composition was found to remain constant during long periods.

A quantity of the alcohol obtained from the rectified spirit was treated several times with anhydrous copper sulphate, and by this means an alcohol of 99 per cent. was obtained. To this was added an excess of metallic calcium, the mixture was boiled for ten hours and finally distilled, the distillate being protected by a phosphoric oxide guard-tube. The density of this alcohol showed that it was anhydrous.

The two esters chosen, ethyl benzoate and ethyl *iso*butyrate, were prepared by the usual methods, and were purified by two fractional distillations, the ethyl benzoate being distilled under diminished pressure.

The hydrochloric acid solutions employed for the titrations were made up in bulk and standardised gravimetrically against silver nitrate. The potassium hydroxide solution showed only a small difference when titrated against the acid, using methyl-orange and phenolphthalein as indicators. Just previous to an experiment, a piece of stick potassium hydroxide was immersed in freshly distilled water, dried between filter-papers, ground up in an agate mortar, and transferred to the alcohol–water mixture. This series of operations was carried out as quickly as possible, and by this means the presence of potassium carbonate was eliminated. The potassium hydroxide solution was then adjusted to the required strength by titration against the standard acid, phenolphthalein being used as indicator.

The experiments were carried out at 30°. The thermostat was gas-heated and maintained at 30°±0·05 by means of a spiral toluene–mercury regulator.



All measuring instruments were calibrated. In the case of the pipettes, a length of capillary tubing was sealed in just above the bulb, the graduation mark occurring about midway in this capillary. The error in delivery of such pipettes is negligible.

In the reaction mixture, about 1·5—2·5 moles of potassium hydroxide were present to one mole of the ester, except in those cases where the influence of the concentration of one of the reactants was being studied.

The course of the reaction was followed by withdrawing 10 c.c. of the reaction mixture and running into standard hydrochloric acid. The amount of hydrochloric acid was regulated by using for the first reading some 3 c.c. less than that calculated to neutralise the potassium hydroxide originally present in 10 c.c. of the reaction mixture; the titration was then completed. At each subsequent reading the amount of hydrochloric acid was reduced in such a manner that about 1 c.c. of the standard acid was required to complete the titration. This amount was estimated by doubling the difference between the two previous titrations. The effect due to the free potassium hydroxide, even in the case of the esters most easily saponified, was negligible, and, further, by this means the cumulative errors due to a double titration were avoided. The indicator used was phenolphthalein.

In alcohol–water mixtures containing less than 30 per cent. of alcohol, the solubility of the ethyl benzoate was so small that the concentrations employed rendered it necessary to take 20 or 25 c.c. samples in order to maintain the sensitiveness of the titrations.

In the neighbourhood of those points where marked changes in the direction of the curve occur, the constant was determined for varying concentrations of one of the reactants and constant concentrations of the other reactant.

The results are shown in the following tables and curves. It is seen from the figures of Table I that, within the limits of experimental error and within the limits examined, the velocity constant is not influenced by changes in the concentration of either of the reactants.

TABLE I.

Ester.	$C_{KOH.}$	$C_{ester.}$	Alcohol per cent.	*k*.
*iso*Butyric	0·05587	0·03333	70	0·124
	0·05587	0·02526	,,	0·112
	0·05587	0·01666	,,	0·122
	0·05587	0·01263	,,	0·122
	0·05500	0·01111	,,	0·116
	0·02438	0·00833	,,	0·112
	0·01760	0·01800	,,	0·115
	0·01543	0·01111	,,	0·117
Benzoic	0·05823	0·03333	80	0·085
	0·05823	0·02222	,,	0·085
	0·02823	0·01111	,,	0·085
	0·01900	0·00952	20	1·22
	0·01198	0·00952	,,	1·27
	0·01900	0·00634	,,	1·17

The value of *k* is, in each case, the mean of some eight determinations. The velocity constant was calculated from the equation (i), where *a* and *b* are the concentrations of the alkali and of the ester respectively, expressed as moles per litre, and *t* is the time expressed in minutes.

In Table II are shown representative results for the saponification of the two esters in given alcohol–water mixtures, indicating the limits between which k varied for any one experiment and the extent to which the saponification was usually carried.

TABLE II.

Ethyl Benzoate.
25 per cent. alcohol.

$a=0{\cdot}02153$; $b=0{\cdot}00853$.
HCl$=0{\cdot}02305N$.

t.	x.10.	k.
30	0·0337	0·84
45	0·0427	0·81
60	0·0516	0·83
75	0·0571	0·82
90	0·0620	0·82
105	0·0660	0·82
120	0·0685	0·80
150	0·0737	0·81
180	0·0772	0·82
		Mean 0·82

Ester saponified$=90{\cdot}6$ per cent.

Ethyl iso*Butyrate.*
85 per cent. alcohol.

$a=0{\cdot}05224$; $b=0{\cdot}03333$.
HCl$=0{\cdot}02367N$.

t.	x.10.	k.
60	0·0644	0·073
90	0·0904	0·072
120	0·1077	0·070
150	0·1219	0·069
180	0·1373	0·073
240	0·1696	0·070
305	0·1933	0·071
360	0·2406	0·071
420	0·2242	0·070
		Mean 0·071

Ester saponified$=67{\cdot}3$ per cent.

The experimental results are shown in tables III and IV.

TABLE III.

Ethyl Benzoate.

Alcohol per cent.	C_{KOH}.	C_{ester}.	Limit k.	k.
100	0·06097	0·03333	0·0016—0·0020	0·00165
97·5	0·05771	,,	0·016 —0·017	0·0165
95	0·04577	0·02222	0·029 —0·0265	0·028
90	0·05770		0·048 —0·0495	0·0485
85	0·04523		0·065 —0·0625	0·0635
82·5	0·05230		0·079 —0·077	0·078
80	0·05823		0·0875—0·0835	0·085
75	0·05893	0·03333	0·089 —0·094	0·0935
70	0·06345	0·02222	0·11 —0·102	0·106
60	0·07140	0·03333	0·128 —0·14	0·133
50	0·06522	0·02222	0·202 —0·210	0·205
46·5	0·06283		0·238 —0·249	0·243
42	0·06170		0·272 —0·284	0·280
40	0·05583		0·283 —0·297	0·290
35	0·04283	0·01333	0·351 —0·361	0·355
30	0·04417	0·01666	0·418 —0·431	0·425
25	0·02153	0·00853	0·81 —0·84	0·82
20	0·01920	0·00952	1·20 —1·25	1·22

TABLE IV.

Ethyl iso*Butyrate.*

Alcohol per cent.	C_{KOH}.	C_{ester}.	Limit k.	k.
100	0·06097	0·03333	0·0016—0·0020	0·00165
97·5	0·05771		0·017 —0·020	0·018
95	0·07112		0·029 —0·033	0·031
90	0·06137		0·049 —0·051	0·050
85	0·05224		0·070 —0·073	0·071
82·5	0·05662		0·079 —0·083	0·081
80	0·06090	0·02222	0·091 —0·095	0·093
75	0·05893	0·03333	0·102 —0·109	0·104
70	0·05500	0·01111	0·111 —0·117	0·116
60	0·05214	0·02222	0·165 —0·182	0·173
50	0·04530	,,	0·225 —0·233	0·230
45	0·03851	0·01666	0·276 —0·290	0·287
40	0·04680	,,	0·321 —0·355	0·350
35	0·01642	0·01333	0·404 —0·426	0·420
30	0·01376	0·00741	0·585 —0·606	0·590
25	0·01226	0·00556	0·79 —0·84	0·81
20	0·01066		1·12 —1·20	1·19

Conclusions.

(1) The reaction is bimolecular and the velocity constant is independent of the initial concentration of the ester or of the alkali.

(2) The curves for ethyl benzoate and for ethyl *iso*butyrate showing the relation between the value of k and the percentage composition of the medium are very nearly parallel.

(3) The curves show that we are dealing with a process divisible into a succession of four phases, and the relation between the value of k and the composition of the solvent is linear for each phase.

(4) The critical points occur at such compositions of the solvent medium that molecular complexes between alcohol and water seem to be indicated.

The authors beg to express their thanks to the Government Grant Committee of the Royal Society for funds placed at their disposal which have defrayed the cost of the research. One of us (A. E. C.) begs to express his thanks to the Department of Scientific and Industrial Research for a grant which has enabled him to collaborate in this work.

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CVII.—*The Influence of Position on the Solubilities of the Substituted Benzoic Acids.*

By Nevil Vincent Sidgwick and Elinor Katharine Ewbank.

It has already been shown (Sidgwick, Spurrell, and Davies, T., 1915, **107**, 1202) that whereas in most di-derivatives of benzene the position of the substituents has little influence on the solubilities in the liquid state, in others, in which the substituents may be presumed to react with one another, this is not the case, and the ortho-compounds behave quite unlike the meta- and para-. The same was found to hold with the vapour pressure of the compounds, either in the pure state, or on distillation with steam (Sidgwick, *ibid.*, 1920, **117**, 389, 396). Substances of the former class were described as normal, those of the latter as abnormal.

Among the substituted benzoic acids, the toluic are strictly normal, while the hydroxybenzoic are markedly abnormal in their vapour pressure, and also, so far as is known, in their solubilities. The object of the present investigation was to examine the solubilities of these and other derivatives of benzoic acid in detail, in a variety of solvents. The acids examined were the hydroxybenzoic, hydroxytoluic, nitrobenzoic, and chlorobenzoic (ortho-, meta-, and para- in each case); the solvents were in all cases water and benzene, and with several acids ethyl and butyl alcohols, and *n*-heptane. For comparison with the mono-substitution products, the solubilities in water and benzene of benzoic, phenylacetic, and β-phenylpropionic acids were also measured.

The solubility of *o*-hydroxybenzoic acid in water has been measured by Alexejeff (*Wied. Ann.*, 1886, **28**, 305), and that of the hydroxy-, nitro-, and chloro-benzoic acids in water by Flaschner and Rankin (*Sitzungsber. K. Akad. Wiss. Wien*, 1909, **118**, II*b*, 695). We were not aware of the latter work until our own was partly finished. Our results with the first two groups are in substantial agreement with theirs; the chloro-acids we did not examine in water. Numerous measurements have been made of the solubilities of these acids at lower temperatures, such as 25°, which do not immediately concern us. One paper, however, by Walker and Wood (T., 1898, **73**, 618), on the hydroxy-acids, although the measurements do not extend beyond 75°, contains results of unusual interest, which are discussed at the conclusion of this paper.

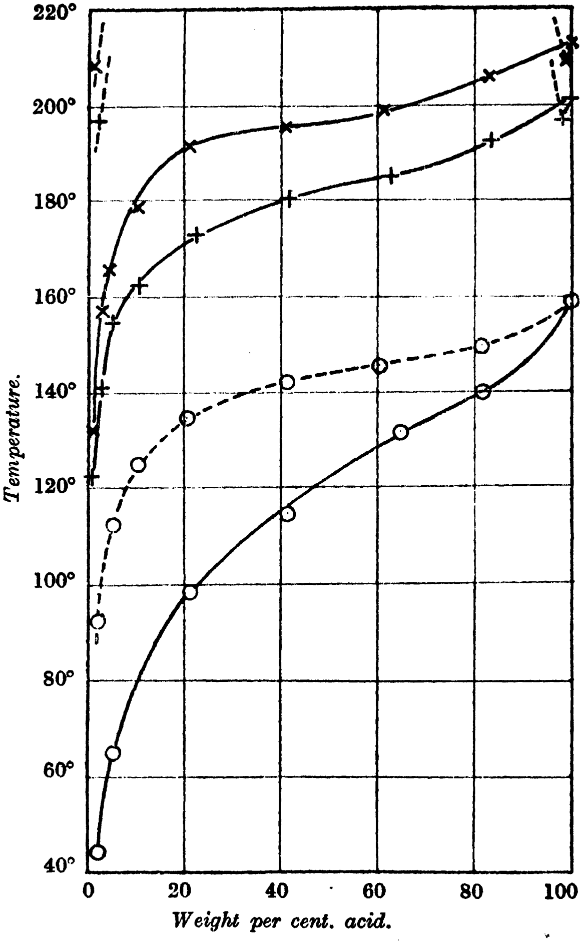


FIG. 1.

Solubility of hydroxybenzoic acids in benzene and heptane.

Ortho — ○ *Full curves* —— *benzene.*
Meta — + *Dotted curves* - - - *heptane.*
Para — ×

EXPERIMENTAL.

Purification of Materials.

The methods by which the acids were prepared and purified have already been described (T., 1920, **117**, 401). Their melting points were as follows:

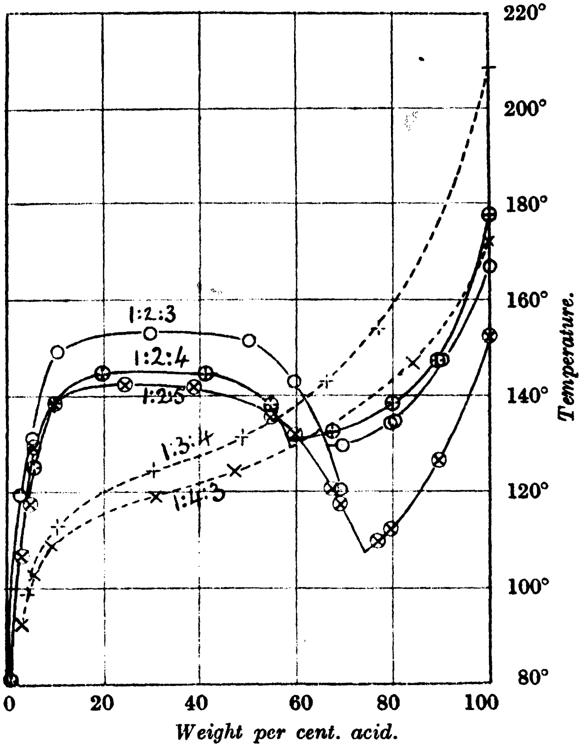
Benzoic, 122·7°; phenylacetic, 76·7°; β-phenylpropionic, 48·6°.
Hydroxybenzoic: ortho-, 159·0°; meta-, 201·5°; para-, 213·0°.
Hydroxytoluic (it is convenient to arrange the substituents in the order of their influence on the properties under discussion):

$CO_2H:OH:CH_3$:	1 : 2 : 3	1 : 2 : 4	1 : 2 : 5	1 : 3 : 4	1 : 4 : 3
Melting point:	167·0°	177·8°	152·5°	208·5°*	172·4°

Nitrobenzoic: ortho-, 146·8°;† meta-, 141·4°; para-, 242·4°.
Chlorobenzoic: ortho-, 140·3°; meta-, 154·5°; para-, 241·5°.

Fig. 2.

Solubility of hydroxytoluic acids in water.



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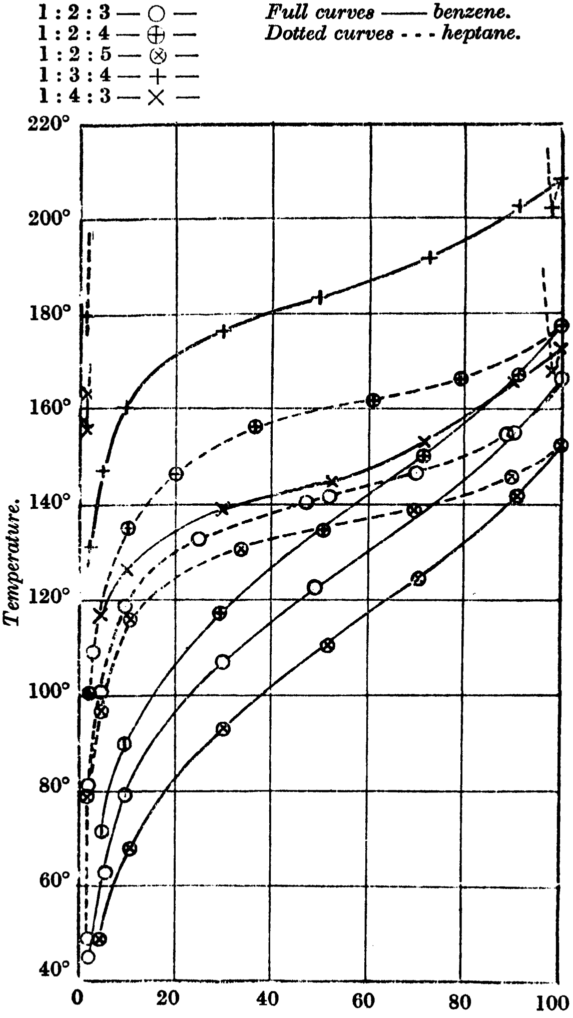
* The melting point obtained for this acid depends on the conditions of experiment, as it begins to decompose above 200°. In a capillary tube, immersed suddenly in an already heated bath, it melts at 208·5°. In the previous paper (*loc. cit.*, p. 402) the melting points of the 1 : 3 : 4- and 1 : 4 : 3-acids were unfortunately transposed.

† Goldschmidt (*Zeitsch. physikal. Chem.*, 1898, **25**, 91) finds the melting point of this acid to be 144·0°, in opposition to the usually accepted value, 147°. We find it to melt sharply at 146·8°.

Of the solvents used, the benzene was freed from thiophen by treatment with sulphuric acid, and frozen out seven times; the ethyl alcohol had been distilled over calcium oxide, and its strength, as measured by the density, was 99·0 per cent.; the *n*-butyl alcohol was repeatedly fractionated, and distilled within 0·1°; the heptane was a specimen from *Pinus sabiniana*, which had been purified

FIG. 3.

Solubility of hydroxytoluic acids in benzene and heptane.



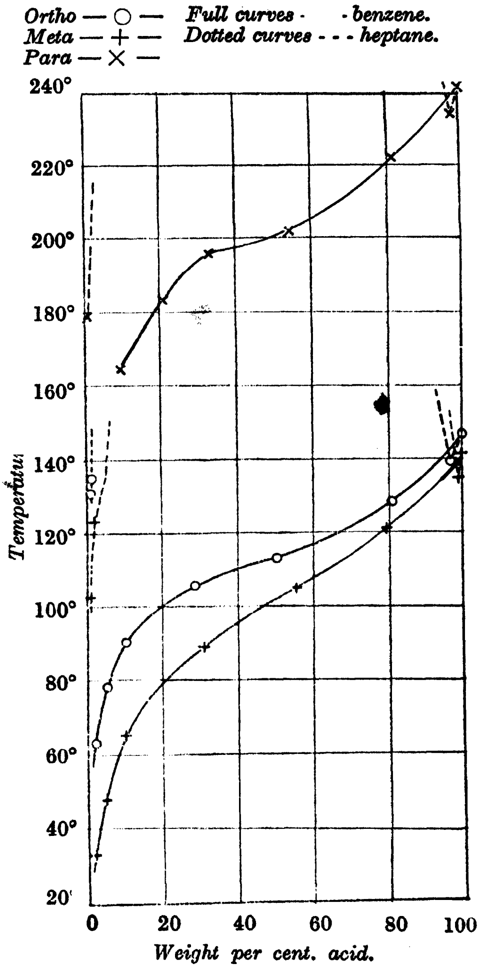
by the method of Thorpe (T., 1879, 35, 296), by treatment with sulphuric and nitric acids, and distillation.

Method of Measurement.

The solubilities were determined synthetically. Weighed quantities of the acid and the solvent were enclosed in bulbs, which were then sealed and heated in a suitable bath. With solvents other than water, a correction was made at higher temperatures for the amount present as vapour in the bulb; for this purpose, the vapour pressure of the saturated solution was assumed to be half that of the pure solvent at the same temperature: a direct measurement of the vapour pressure of a saturated solution of *m*-hydroxybenzoic acid in benzene showed that between 160° and 210° this assumption is sufficiently near the truth. The thermometers had been compared with a standard instrument, and all readings were corrected for the emergent stem. The concentrations are expressed in grams of acid to 100 grams of solution.

FIG. 4.

Solubility of nitrobenzoic acids in benzene and heptane.



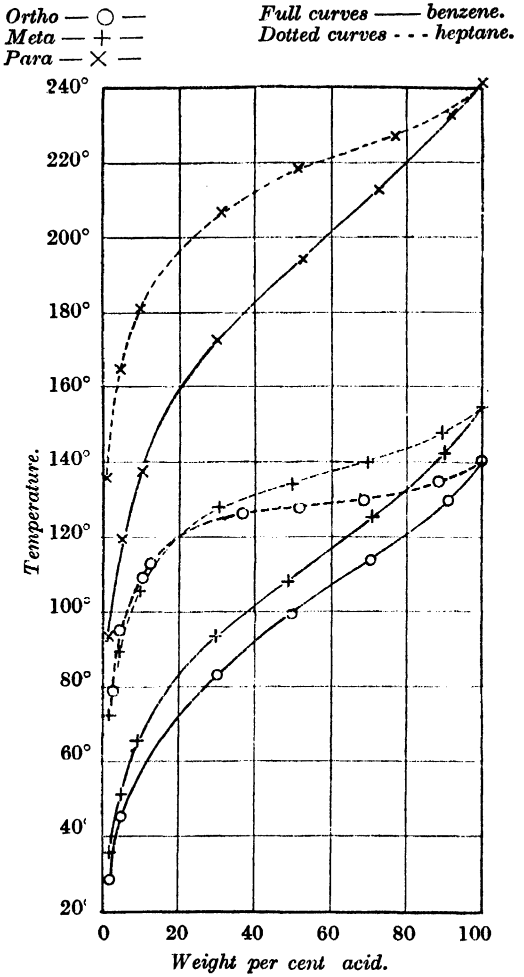
The results are given in Table I, and plotted on Figs. 1—6. One or two points may be added.

p-Hydroxybenzoic acid crystallises with a molecule of water (the concentrations, of course, refer to the anhydrous acid). The transition point was determined in a dilatometer with water, and was found to be 62·0°. The solubility values confirm this result; a distinct break is to be observed in the curve at this temperature.

1 : 4 : 3-Hydroxytoluic acid also forms a hydrate, with half a molecule of water. The transition point, as shown by the solubility curve, is 99·5°.

FIG. 5.

Solubility of chlorobenzoic acids in benzene and heptane.



In heptane, the acids the solubility of which is small, appeared to decompose very little above their triple points, and so the curves were not carried further.

The determinations with benzoic acid and water were only intended to supplement the results of Alexejeff (*loc. cit.*). As will be seen from Fig. 6, our results agree with his as regards the critical solution temperature, but we find the triple point to be 95·0°, and not, as he states, 98°.

FIG. 6.

Solubility of benzoic, phenylacetic, and β-phenylpropionic acids in water and benzene.

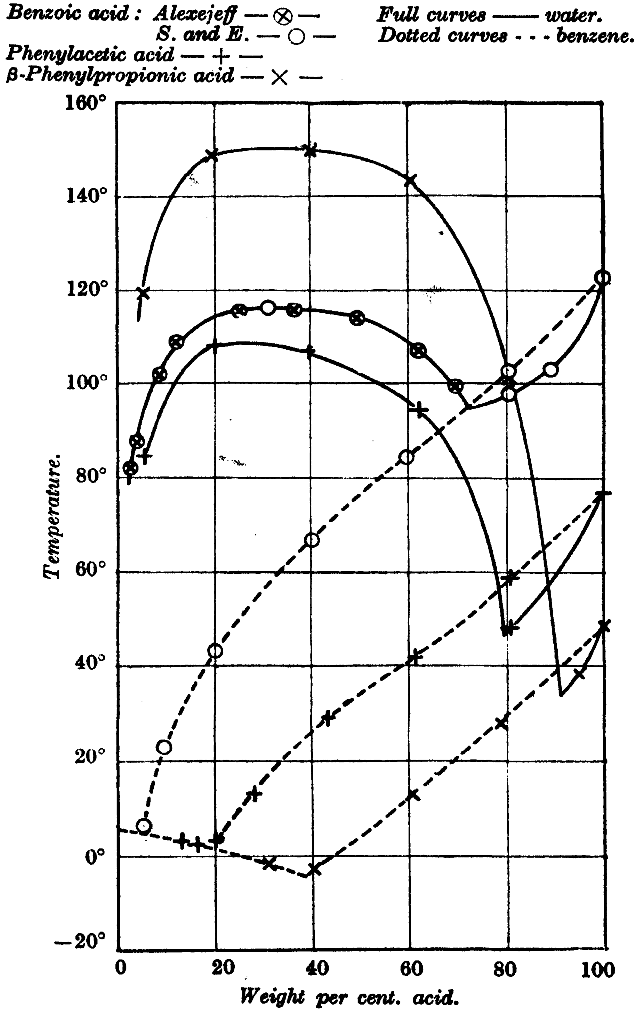


TABLE I.

(All solubilities are expressed in grams of acid to 100 grams of solution).

A. *Hydroxybenzoic Acids.*

Ortho-.			Meta-.		Para-.	
Solʸ.	Temp. (Solid).	Temp. (Liquid.)	Solʸ.	Temp.	Solʸ.	Temp.
			Solubility in Water.			
100·0	159·0°		100·0	201·3°	100·0	213·0°
89·75	131·8		70·80	134·0	85·20	167·0
80·00	119·5		49·85	109·8	71·30	137·5
65·40	109·5	67·0°	33·85	98·3	51·95	114·0
48·18	107·2	86·4	25·22	93·3	46·60	109·5
34·02	106·7	89·1	14·70	84·6	29·47	97·0
16·82	105·6	87·2	9·85	79·6	19·66	89·6
8·02	101·4	77·3	6·11	69·0	11·85	80·1
5·27	97·9				9·28	75·7
2·026	80·0				6·07	68·2
0·717	56·0				5·22	65·1
0·557	50·0				4·75	63·0
Critical solution temp.		89·5°			4·20	60·2
					3·20	56·0
					2·38	50·9
					Transition point of hydrated acid ...	62·0°
			Solubility in Ethyl Alcohol (99·0%).			
100·0	159·0		100·0	201·3	100·0	213·0
81·2	125·2		81·7	169·0	82·9	184·0
60·4	85·2		61·3	132·0	60·9	136·5
40·6	41·0		39·6	65·0	38·75	67·0
			Solubility in *n*-Butyl Alcohol.			
79·2	121·6		84·7	180·3	85·5	193·8
48·9	85·6		59·2	151·2	62·4	167·0
28·88	38·0		40·8	115·0	39·45	116·1
24·36	24·0		20·7	36·5	25·08	62·0
					19·50	32·5
			Solubility in Benzene.			
100·0	159·0		100·0	201·3	100·0	213·0
81·3	140·0		83·3	192·5	83·0	206·0
64·5	131·5		62·3	185·5	61·3	198·8
41·1	114·5		41·6	182·5	40·6	195·7
20·8	98·5		22·4	173·0	21·0	191·5
5·27	65·0		10·54	162·0	10·3	178·0
1·92	44·3		5·16	154·5	4·30	165·3
			2·95	141·0	3·03	156·9
			1·23	122·5	1·04	132·2
			Solubility in *n*-Heptane.			
81·4	149·5		2·00	197·0(liq.)	1·80	208·5(liq.)
60·2	145·5		0·86	176·0	1·06	197·0
41·6	142·0		Triple point	197·0°	Triple point	208·5°
20·15	134·3					
10·25	124·7					
5·37	112·4					
2·09	92·2					

TABLE I. (*continued*).

B. *Hydroxytoluic Acids.*

(Points at which a second liquid layer separates are marked L.)

Solubility in Water.

$CO_2H : OH : CH_3$ 1 : 2 : 3		$CO_2H : OH : CH_3$ 1 : 2 : 4		$CO_2H : OH : CH_3$ 1 : 2 : 5		$CO_2H : OH : CH_3$ 1 : 3 : 4		$CO_2H : OH : CH_3$ 1 : 4 : 3	
Sol^y.	Temp.	Sol^y.	Temp.	Sol^y.	Temp.	Sol^y.	Temp.	Sol^y.	Temp.
100·0	167·0°	100·0	177·8°	100·0	152·5°	100·0	208·5°	100·0	172·4°
90·07	147·5	89·68	147·8	89·71	126·4	76·98	154·0	84·12	146·8
80·50	134·5	79·68	138·3	79·66	112·0	66·07	143·0	65·52	132·4
79·68	134·1	67·68	132·6	77·05	109·5	48·67	131·4	47·57	124·1
69·52	129·8	54·40	130·4(L)	69·29	117·7(L)	30·23	124·2	30·87	118·8
,,	120·3(L)	41·46	144·6(L)	67·91	120·2(L)	10·33	113·1	9·61	109·0
59·73	143·0(L)	19·89	144·6(L)	59·85	131·5(L)	4·03	98·8	6·52	105·8
50·51	151·3(L)	9·75	138·4(L)	55·16	135·6(L)			5·77	103·4
29·81	153·3(L)	5·53	129·4	38·85	142·0(L)			5·01	99·5
10·18	149·3(L)	,,	125·3(L)	24·55	142·5(L)			3·70	96·6
5·07	131·8(L)	0·412	80·7	10·21	138·5(L)			2·77	92·6
2·20	119·1			4·53	117·5(L)			1·83	84·4
0·364	80·7			3·16	107·0				
				,,	106·8(L)				
				0·92	85·0				
				0·73	80·7				
Triple point	129·2°		131·0°		107·8°	Transition point of hydrate			99·5°
Critical solution temp.	153·5°		145·2°		142·8°				

Solubility in Benzene.

$CO_2H : OH : CH_3$ 1 : 2 : 3		$CO_2H : OH : CH_3$ 1 : 2 : 4		$CO_2H : OH : CH_3$ 1 : 2 : 5		$CO_2H : OH : CH_3$ 1 : 3 : 4		$CO_2H : OH : CH_3$ 1 : 4 : 3	
90·33	155·4	91·6	167·6	91·10	142·0	91·7	202·5	90·7	166·0
69·92	138·3	71·7	150·3	70·36	124·7	72·7	192·0	71·7	152·8
49·18	123·0	50·7	135·1	52·05	110·6	50·0	183·7	52·6	145·0
29·96	107·2	29·33	117·6	29·98	93·3	29·8	176·5	29·8	139·5
9·67	79·1	9·74	90·2	10·53	68·0	9·80	160·5	10·11	126·2
5·23	62·4	4·96	71·7	4·73	48·8	4·87	147·4	4·78	116·7
2·01	45·2	2·02	48·8	1·76	30·0	2·18	131·6	2·78	109·5

Solubility in *n*-Heptane.

$CO_2H : OH : CH_3$ 1 : 2 : 3		$CO_2H : OH : CH_3$ 1 : 2 : 4		$CO_2H : OH : CH_3$ 1 : 2 : 5		$CO_2H : OH : CH_3$ 1 : 3 : 4		$CO_2H : OH : CH_3$ 1 : 4 : 3	
100·0	167·0	100·0	177·8	100·0	152·5	100·0	207·0	100·0	172·4
88·95	154·3	79·29	166·7	89·9	145·9	0·94	180	1·40	163·8
70·04	146·6	61·03	162·2	69·9	138·7			,,	156·0(L)
52·03	141·9	36·28	156·6	50·9	135·5			1·02	157·3
47·63	140·0	20·15	147·1	30·38	131·1			,,	135·0(L)
24·77	132·9	10·00	135·6	10·42	116·2				
9·95	119·0	4·51	116·7	4·59	97·1				
4·86	101·0	2·12	100·6	1·84	79·0				
1·89	81·0								
						Triple point	202°	Triple point	163°

C. *Nitrobenzoic Acids.*

Solubility in Water.

Ortho-.		Meta-.		Para-.	
Sol^y.	Temp.	Sol^y.	Temp.	Sol^y.	Temp.
100·0	146·8°	100·0	141·4°	100·0	242·4°
90·38	110·4	89·76	104·8	79·22	184·8
79·32	90·5	79·52	85·4	59·21	168·6
59·85	79·5	60·85	97·7(L)	38·30	163·5
39·92	78·0	40·31	108·4(L)	18·50	158·8
19·24	77·5	19·85	107·8(L)	9·17	153·0
9·48	75·3	9·90	99·3(L)	0·88	177·0
1·85	49·5	4·57	79·3(L)		
		Triple point	76·8°		
		Critical solution temp.	109·0°		

TABLE I. (*continued*).

Solubility in Benzene.

Sol^y^.	Temp.	Sol^y^.	Temp.	Sol^y^.	Temp.
100·0	146·8	100·0	141·4	100·0	242·4
81·00	128·3	79·6	121·0	82·1	222·0
50·25	113·0	55·5	105·0	54·8	201·6
28·32	105·8	30·54	89·5	33·42	196·5
10·00	90·5	9·87	65·2	21·10	183·4
5·03	78·6	4·95	48·0	9·45	164·5
2·10	63·0	1·95	33·0		

Solubility in Heptane.

1·37	135·0	2·07	123·4	1·04	179·0
,,	130·5(L)	1·03	103·0		
Triple point	139·6°		135°		234·0°

D. *Chlorobenzoic Acids.*

Solubility in Benzene.

Ortho-.		Meta-.		Para-.	
100·0	140·3	100·0	154·5	100·0	241·5
90·9	129·5	90·2	142·5	92·2	232·5
70·4	113·9	71·15	125·3	72·9	212·7
50·08	99·6	49·0	108·0	52·5	194·0
29·81	82·7	30·1	93·7	30·5	172·5
9·91	57·7	9·67	65·5	10·30	137·4
5·15	44·8	4·96	51·2	5·30	119·4
1·98	26·0	2·25	35·8	1·98	93·6

Solubility in *n*-Heptane.

88·68	134·7	89·82	147·7	76·86	227·6
68·76	129·8	70·05	140·1	51·30	218·3
51·90	128·0	50·06	134·2	31·23	207·2
36·89	126·0	30·60	128·1	10·09	180·9
12·55	112·8	9·98	105·8	4·96	165·3
10·42	108·8	4·48	89·6	1·69	136·1
4·61	94·8	1·92	72·2		
2·57	79·0				

E. *Benzoic Acid.* F. *Phenylacetic Acid.* G. β-*Phenylpionic Acid.*

Solubility in Water.

Sol^y^.	Temp.	Sol^y^.	Temp.	Sol^y^.	Temp.
100·0	122·7°	100·0	76·7°	100·0	48·6°
89·40	103·5	80·96	48·5	94·92	38·5
80·36	98·0	61·94	94·8(L)	80·30	101·5(L)
,,	77·8(L)	39·69	106·8(L)	60·16	143·5(L)
30·78	116·2(L)	20·00	108·0(L)	39·31	150·0(L)
		5·65	84·7(L)	19·31	149·2(L)
				5·00	119·9(L)
Triple point	95·0°		45·5°		34·0°
Critical solution temp.	115·5°		108·0°		150·0°

TABLE I. (*continued*).

Solubility in Benzene (Points where benzene separates marked B).

Sol^y.	Temp.	Sol^y.	Temp.	Sol^y.	Temp.
100·0	122·7	100·0	76·7	100·0	48·6
80·5	103·0	81·03	59·0	78·87	28·0
59·70	84·4	61·28	42·0	60·43	+12·8
40·12	66·7	42·98	29·0	40·20	−3·1
20·08	43·5	28·00	13·0	31·26	−1·8(B)
9·40	23·0	19·93	3·0	19·65	+1·5(B)
4·92	6·5	16·30	2·2(B)	0·0	+5·5(B)
		13·04	3·2(B)		
		6·22	4·6(B)		
		0·0	5·5(B)		

Interpretation of Results.

It has already been pointed out that the properties of a crystalline substance are due to two causes: those depending on the molecule itself, and those which arise from the crystalline forces; and that quite small differences in structure (such as those between the isomerides of a normal group), which have practically no effect on the behaviour of the fused or dissolved substance, may lead to a large difference in any property in which the solid phase is concerned. If, therefore, we are to discover the effect of position on the properties of the molecule, we must eliminate the influence of the crystalline forces, by considering the solubility in the liquid state. This is best characterised by the critical solution temperature (the temperature at which the fused substance and the solvent become infinitely miscible), whenever this can be determined. In many cases the L_1—L_2 equilibrium is stable, and the critical solution temperature can be observed directly, if it is not too high. With other substances, this curve is wholly metastable: it lies entirely below the S—L curve; but if it is not too far below, it may be possible to realise it experimentally, as happens with salicylic acid, where the solution, supersaturated with respect to the solid acid, separates into two liquid layers before crystallisation begins. With other substances, however, the L_1—L_2 area lies too low for this, and crystallisation always sets in before it can be reached. An ingenious method has been devised by Flaschner and Rankin (*loc. cit.*) for dealing with such cases. A third substance, miscible with the acid rather than with the solvent, is added to a mixture containing about 40 per cent. of the acid (this is roughly the composition at the critical solution point); this raises the temperature of the L_1—L_2 curve, until finally the two-liquid system can be realised. If several measurements are made with different quantities of the third substance, and these quantities plotted against the temperatures of separation, they are found to give nearly a straight line, at least when the amount of the third substance is small; and from this by extrapolation the temperature for no addition—the critical solution temperature for acid and solvent—can be obtained. This method gives only approximate results, and is naturally less accurate the larger the extrapolation required; but it is of considerable value. Flaschner and Rankin employed it in a series of instances in aqueous solution, using chiefly naphthalene, but also benzil, benzophenone, and camphor, as the third substance. We find that where the solvent is water, sodium chloride can be used as the third substance. Thus with *p*-nitrobenzoic acid in water, Flaschner and Rankin, using benzophenone, obtained the following values, which extrapolate to 118° for the critical solution temperature (the third line, *dt/dw*, gives the quotient of rise of temperature above the extrapolated point by weight per cent. added, and its constancy shows the closeness with which the results approach to a straight line):

Benzophenone per cent.	10·9	7·9	6·7	5·8	(0·0)
Separation temp..........	172°	157°	151°	147°	(118°)
dt/dw	5·0°	4·9°	4·9°	5·0°	—

Our own results with sodium chloride extrapolated to practically the same point:

Salt per cent.	7·99	7·04	6·03	(0·0)
Separation temp.......	179·5°	173·5°	164·4°	(118°)
dt/dw	7·7°	7·9°	7·7°	—

When the solvent is benzene, it is not easy to select a suitable third substance, which should be readily miscible with one component, and little, if at all, with the other. Unexpectedly good results were, however, obtained with water, as is shown below (the values of *dt/dw* are calculated back from the extrapolated value of the critical solution temperature):

o-Hydroxybenzoic acid in benzene:

Water per cent.	6·97	6·21	4·98	(0·0)
Separation temp.......	121·5°	110·5°	91·6°	(+17°)
dt/dw	15·0°	15·1°	15·0°	—

m-Hydroxybenzoic acid in benzene:

Water per cent.	(9·20)	6·25	4·10	(0·0)
Separation temp.......	(189·0°)	169·8°	152·0°	(119°)
dt/dw	(7·6°)	8·0°	8·0°	—

p-Hydroxybenzoic acid in benzene:

Water per cent.	5·46	4·11	3·36	(0·0)
Separation temp.......	187·0°	177·5°	172·5°	(150°)
dt/dw	6·8°	6·7°	6·7°	—

m-Nitrobenzoic acid in benzene:

Water per cent.	6·72	4·86	3·12	(0·0)
Separation temp.......	118·0°	82·0°	50·0°	(−9°)
dt/dw	18·9°	18·7°	18·9°	—

In heptane, with *o*-hydroxybenzoic acid, less satisfactory results were obtained:

Water per cent.	4·14	2·00	1·47	0·96	(0·0)
Separation temp.......	189·5°	154·0°	141·0°	124·0°	(90°)
dt/dw	24°	32°	35°	35°	—

The zero value of 90° was got from the two lowest observations; it gives an upper limit for the critical solution temperature.

When the critical solution temperature cannot be obtained in this way, another, less accurate, method may be used, depending on the slope of the *S*—*L* solubility curve. It is obvious that the middle part of this is flatter, the nearer it lies to the L_1—L_2 curve. In aqueous solutions (and in one or two cases in other solvents also), Flaschner and Rankin found that if the slope of this curve (increase in weight per cent. for 1° rise of temperature) at 40 per cent. solute is multiplied by the difference in temperature at this concentration between the *S*—*L* and the L_1—L_2 curves, it gives a number (*E*) which is approximately constant. For eleven substituted benzoic acids in water they found values of *E* varying from 520 to 189 (mostly between 250 and 360), with a mean value of 330. With benzene or heptane as solvents, we have obtained the following values (the first column gives the slope of the *S*—*L* curve, the second the difference in temperature between the two curves at 40 per cent. acid, the third, *E*, the product of these two):

	dc/dt	*Dt*	*E*
Hydroxybenzoic acid, ortho- in benzene	1·62	98·8°	160
,, ,, meta- ,, ...	2·76	57·3	157
,, ,, para- ,, ...	5·78	45·5	263
,, ,, ortho- in heptane ...	3·72	52·0	193
Nitrobenzoic acid, ortho- in benzene	3·21	130·8	[420]
,, ,, meta- ,, ...	1·70	106·0	180
		Mean	190

It will be seen that the values obtained in non-dissociating solvents agree about as closely as those in water, and give a distinctly lower mean.* It is difficult to see any quantitative theoretical basis for this rule, but the agreement is close enough for it to be worth while examining the results got by applying it to cases where the two-liquid curve lies too low to be reached even by salting out; and they have therefore been calculated in such cases, using the mean value 330 for *E* in water, and 190 in benzene and heptane. In Table II, all the values of the critical solution temperatures obtained by any of the three methods are collected, the method employed in each case being indicated. It is obvious that little weight can be attached to the absolute magnitude of the temperatures obtained

* The value for *o*-nitrobenzoic acid is excluded in calculating the mean.

TABLE II.

Critical Solution Temperatures.

(Obs.=by direct observation. S.O.=by method of salting out. Calc.=calculated by the formula of Flaschner and Rankin from the slope of the *S*—*L* curve, using *E*=330 for water, and 190 for benzene and heptane.)

Acid	Solvent.	Ortho-.	Meta-.	Para-.
Hydroxybenzoic	water	89·5° Obs.	−122° Calc.	−229° Calc.
	ethyl alcohol butyl alcohol	v. low	v. low	v. low
	benzene	+17° S.O.	119° S.O.	150° S.O.
	,,	(−6° Calc.)	(114° Calc.)	(162° Calc.)
	heptane	90° S.O.	v. high	v. high
	,,	(91° Calc.)		
Nitrobenzoic	water	52° S.O.*	109·0 Obs.	118° S.O.
	benzene	−21° S.O.	−9° S.O.	
	,,	(+53° Calc.)	(−16° Calc).	+84° Calc.
	heptane	v. high	v. high	v. high
Chlorobenzoic	water	126·2° Obs.*	142·8° Obs.*	167·0° Obs.*
	benzene	−52° Calc.	−36° Calc.	−13° Calc.
	heptane	+99° Calc.	+75° Calc.	+123° Calc.

Hydroxytoluic (CO_2H:OH:CH_3)	Solvent.	1 : 2 : 3-	1 : 2 : 4-.	1 : 2 : 5-.	1 : 3 : 4-.	1 :4 : 3-
	water	153·5° Obs.	145·2° Obs.	142·8° Obs.	+9° Calc.	+17° Calc.
	benzene	−33° Calc.	−16° Calc.	−47° Calc.	+117° Calc.	+98° Calc.
	heptane	+84° Calc.	+111° Calc.	+107° Calc.	v. high	v. high

Solvent.	Benzoic acid.	Phenylacetic acid	β-Phenylpropionic acid.
Water	116·2° Obs.	108·0° Obs.	150·0° Obs.
Benzene	v. low	v. low	v. low

by the third method—indeed, with the alcohols they come below the absolute zero—but they show on the whole a remarkable regularity, and indicate that there is some definite relation between the slope of the solid solubility curve and its distance from the two-liquid curve, although the exact form of the function is not yet known.

Nominal Heats of Solution.

In solvents other than water, the critical solution temperatures usually cannot be determined, except by large interpolations with uncertain formulæ, and we have to rely on the solid solubility curves alone. The differences between these are much less easy to detect. The curves seem to be governed by the melting points and heats of fusion of the solid acids (properties depending mainly on the crystalline forces) and it is not easy to see how far their course departs from the normal. A much clearer view is afforded by plotting the heats of solution against the concentration. As van't Hoff has shown,† it is possible, if we know the solubility of a solid in a solvent at two temperatures, to calculate the mean heat of solution (in the saturated solution) by means of the equation:

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* These observations are due to Flaschner and Rankin, *loc. cit.*

† See also Schröder, *Zeitsch. physikal. Chem.* 1893, **11**, 449.

$$\log_e \frac{S}{S_1} = \frac{Q}{1{\cdot}985} \times \frac{T_1 - T}{TT_1},$$

where S, S_1 are the solubilities (expressed as molecular concentrations) at the absolute temperature T, T_1, and Q is the heat of solution. This equation was applied by interpolating values of the temperature on the solubility curves for every 10 (molecular) per cent., calculating the heats of solution between each successive pair, and plotting the results against the concentration. The values so obtained are given in tables III and IV, and those in benzene plotted on Fig. 7.

It must be noticed that this equation only holds on two assumptions: (1) that the solutions obey the gas laws, and (2) that no changes of molecular weight occur with change of concentration. As neither of these assumptions can be supposed to hold throughout, the results do not really represent the heat of solution, and we have therefore called them the nominal heats of solution. They are, however, of considerable importance as affording an expression of the total departure of the liquid system from the behaviour of an ideal solution. With such a solution, the solubility curve is entirely determined by the melting point and heat of fusion of the solid, and is independent of the solvent. In this case the curve gives the real (and not merely the nominal) heat of solution, which is the sum of the heat of fusion of the solid and the heat of mixture of the resulting liquid with the solvent. For ideal components which give a straight line vapour pressure curve the heat of mixture is zero (Bose, *Zeitsch. physikal. Chem.*, 1907, **58**, 621), and hence the value obtained is that of the heat of fusion. This varies with the temperature, its coefficient being equal to the difference between the specific heats of the liquid and solid. It was shown by van't Hoff (Boltzmann, *Festschrift*, 1904, 233) that the specific heat of a substance is always less in the solid state than when it is melted; and this has subsequently been recognised as a necessary consequence of Nernst's theorem. The difference, however, is usually small. From the list of thirteen organic substances * given by van't Hoff (most of which are taken from the results of Bruner, *Ber.*, 1894, **27**, 2102), it appears that the difference is nearly always less than 0·02 kgr.-cal. per gram-molecule per degree; its mean value is 0·013. This means that the heat of fusion will always fall with the temperature, but that 50° below the melting point it will have diminished on the average by not more than 0·65 kgr.-cal., and only in exceptional cases by as much as 1 kgr.-cal. The influence of this factor is also regular; it will cause a small continuous fall of the heat curve. For example, the specific heat of solid benzoic acid is 0·27 cal. per gram, and that of the liquid 0·37 (van't Hoff); this corresponds with a fall of 0·0122 kgr.-cal. per gram-molecule per degree. The solubility in benzene was measured from the melting point (122·7°) down to +6°. The heat of fusion at the melting point being 4·83 kgr.-cals., it will have fallen at 6° to 3·41. With phenylacetic acid, the fall is from 4·3 at the melting point to

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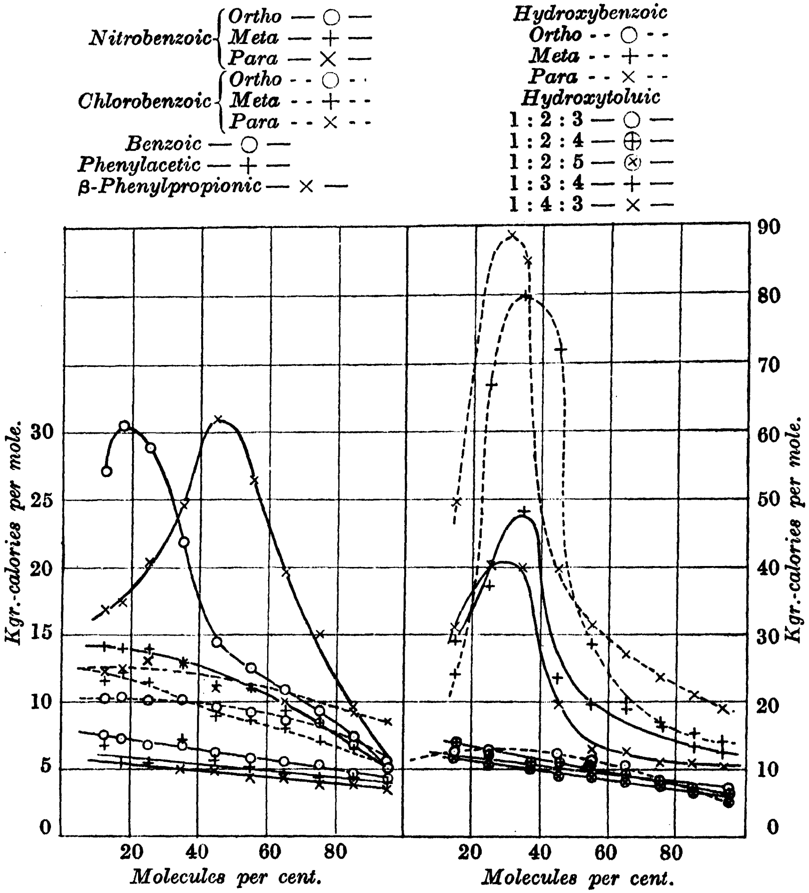
* To these may be added anthracene and triphenylmethane, for which the differences are 0·009 and 0·016 kgr.-cal. per molecule per degree respectively (Hildebrand, Derschak, Foster, and Beebe, *J. Amer. Chem. Soc.*, 1917, **39**, 2293).

FIG. 7.

Heats of solution in benzene.



2·7 at the lowest temperature (+3°) at which the solubility was measured.

The heat of solution for an ideal pair of components will therefore approximate to a horizontal straight line. Such a pair can, of course, never separate into two layers. At the other extreme, we have those substances which "melt under the solvent," where the two-liquid area is stable, and cuts across the *S*—*L* curve. The latter then runs horizontally between the two triple points, and over this range the nominal heat of solution is infinite. The cases which in practice it is important to distinguish are the intermediate ones, in which the *S*—*L* curve shows a certain amount of flattening, indicating that there is an unstable two-liquid area some way below it. Any such flattening is represented on the heat curve by a large increase, and the departures from the normal become much more conspicuous. The value of this method of representation is well shown by comparing the solubility curves of the nitro- and chloro-benzoic acids in benzene (figs. 4, 5) with the corresponding curves (Fig. 7) for their nominal heats of solution. The former do not indicate clearly whether the behaviour of the isomerides in either case is similar or not, whilst from the heat curves it is at once apparent that the chloro-acids are normal and the nitro-acids abnormal.

This method of treatment * is based on the same principles as the calculation of the critical solution temperatures from the slope of the *S*—*L* curve, but it has a firmer theoretical basis, and avoids the somewhat arbitrary selection of a particular concentration. Both methods ultimately depend on the variation of the vapour pressure of one component in the solution with the concentration.

Vapour Pressure of the Liquid Acids.

The vapour pressures of these acids have been determined by means of their volatility in steam (Sidgwick, T., 1920, **117**, 396). This gives the partial pressure of the acid in the vapour from the saturated aqueous solution at 100°, that solution being in equilibrium either with the solid acid or with a second liquid phase, according as the triple point is above or below 100°. In order to compare the properties of the liquid substances, we require to know the vapour pressures of the pure liquid acids, and therefore to eliminate the effect upon them of their dilution by the solvent. When the solid acid is present, the vapour pressure measured is that of the solid; and from this we can calculate that of the pure liquid at

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* For a further discussion of solubility from the point of view of the heat relations, see Hildebrand, *J. Amer. Chem. Soc.*, 1916, **38**, 1451, 2297.

TABLE III.

Nominal Heats of Solution in Benzene (Kgr.-cals. per gram-mol.)

Mean mol. per cent. of acid.	Hydroxybenzoic acids.			Hydroxytoluic acids.				
	Ortho-.	Meta-.	Para-.	1 : 2 : 3-.	1 : 2 : 4-.	1 : 2: 5-.	1: 3 : 4-.	1 : 4 : 3-.
95	5·01	14·3	19·0	7·17	6·71	6·00	12·6	10·9
85	6·51	15·7	21·1	7·50	7·62	6·79	13·5	11·2
75	8·67	17·0	23·6	8·41	8·40	7·74	16·4	11·2
65	10·8	20·0	27·0	8·68	9·43	8·39	19·2	12·7
55	11·5	28·5	31·5	10·1	10·8	8·90	19·6	13·2
45	12·5	71·9	39·7	10·5	11·0	9·08	23·6	19·8
35	11·7	79·9	84·6	10·4	11·3	10·2	48·0	40·3
25	13·0	66·9	88·8	11·4	12·2	10·6	37·0	40·0
15	12·8	24·1	49·7	12·7	14·2	12·4	29·1	31·0
Heat of Fusion......	4·2	11·5	(18·2)	7·0	6·2	5·6	7·26*	10·6

Mean mol. per cent. of acid.	Nitrobenzoic acids.			Chlorobenzoic acids.			Benzoic acid.	Phenyl-acetic acid.	β-Phenyl-propionic acid.
	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.			
95	5·18	5·44	5·99	4·88	5·15	8·68	4·59	4·34	3·60
85	7·42	6·71	9·70	6·91	6·46	9·17	4·75	4·40	3·87
75	9·27	8·31	15·0	8·41	7·11	9·95	5·34	4·43	3·90
65	10·9	9·36	19·7	8·60	8·10	9·96	5·61	4·70	4·46
55	12·6	9·12	26·4	9·22	8·60	11·0	5·81	5·16	4·33
45	14·4	11·0	30·9	9·62	8·94	11·2	6·32	5·72	4·84
35	21·8	12·3	24·6	10·2	10·1	12·9	6·72	7·21	5·02
25	28·8	13·9	20·4	10·1	11·4	13·1	6·87	5·45	—
17·5	30·5	13·9	17·3	10·3	12·5	12·3	7·34	5·51	—
12·5	27·2	14·2	16·9	10·2	11·6	12·3	7·60	6·90	—
Heat of Fusion......	7·34*	5·11*	(5·0)	3·8	4·2	(8·4)	4·83*	4·3	3·5

TABLE IV.

Nominal Heats of Solution in Heptane.

Mean mol. per cent. of acid.	o-Hydroxy-benzoic acid.	Hydroxytoluic acids.			Chlorobenzoic acids.		
		1 : 2 : 3-.	1 : 2 : 4-.	1 : 2 : 5-.	Ortho-.	Meta-.	Para-.
95	7·56	4·05	8·08	7·64	9·57	7·87	11·4
85	11·7	9·52	12·8	11·4	13·9	11·5	13·4
75	22·5	13·6	19·8	11·7	19·9	14·9	17·2
65	31·9	17·5	26·8	20·1	29·4	18·2	21·9
55	45·3	27·5	34·4	32·1	53·3	21·9	29·7
45	51·4	33·3	39·7	49·4	89·2	26·4	29·9
35	39·4	31·4	39·4	52·7	65·3	29·4	26·9
25	35·1	30·6	30·1	37·7	44·0	31·7	23·1
17·5	31·8	25·4	22·7	33·0	31·9	22·1	21·5
12·5	25·3	27·6	22·1	24·1	23·7	14·4	20·0
7·5	18·6	14·0	16·7	15·0	15·7	13·9	20·4

Hydroxybenzoic, meta- and para- Hydroxytoluic, 1 : 3 : 4- and 1 : 4 : 3- Nitrobenzoic, ortho-, meta-, para-	Heat infinite (two layers).

Nominal Heats of Solution of Hydroxybenzoic Acids in Alcohols.

Mean mol. per cent. of acid.	in Ethyl alcohol.			in Butyl alcohol.		
	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.
95	6·40	7·74	8·57	6·00	5·64	6·07
85	5·69	6·71	8·18	5·45	5·94	6·72
75	5·21	6·43	7·23	5·08	6·34	7·59
65	4·68	6·26	6·25	5·17	7·22	7·66
55	4·48	5·61	5·61	4·63	7·09	7·62
45	3·88	5·27	4·70	4·12	6·66	5·95
35	3·44	4·92	3·78	3·39	4·63	4·17
25	3·05	2·90	2·75	2·97	2·76	2·54
17·5	1·19	1·54	1·78	—	2·32	2·79

the same temperature if its heat of fusion is known, the two being related by the formula

$$2{\cdot}3026 \log \frac{p}{p'} = \frac{1000\,W}{R} \times \left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where p, p' are the vapour pressures of liquid and solid at T, the absolute temperature of distillation, and W is the heat of fusion in kgr.-cals. per gram-molecule, T_0 being the melting point. When the substance melts in contact with water below 100° and there are two liquid phases present, an approximate correction can be arrived at in this way. At the triple point (which in this case is below 100°), we can calculate the value of p/p' as before, and hence we know how much the vapour pressure of the acid is diminished by the amount of water dissolved in it at this point. Further, we know that the vapour pressure is the same for the conjugate solution at the other triple point on the dilute side. Nearly the same relations hold for temperatures and concentrations lying outside the two-liquid area, but not too far from it. Over this range the vapour pressure changes very slightly with the concentration. The proportion of acid in the saturated liquid at 100° will not be much less than at the triple point; and hence we shall not be far wrong if we assume that the vapour pressure of the pure liquid acid is lowered to the same relative extent by the amount of water dissolved in it at 100° as it is by the amount dissolved at the triple point. The corrected values for the pure fused acid are therefore obtained by multiplying the observed vapour pressures by the ratio $p_{\text{liquid}}/p_{\text{solid}}$ at 100° when the solid acid is present during the distillation, and by the same ratio at the triple point when two liquid phases are present. The results are given, together with the observed vapour pressures, in Table V.

The heats of fusion required for this purpose have been obtained in most cases by extrapolation from the Q-curves in benzene. These give satisfactory values for the acids of the ortho-group, for which these curves are normal. They are less satisfactory with the meta- and para-compounds, for which the Q-curves show a large rise. The acids melting in the neighbourhood of 200° begin to decompose near this temperature, and the observed melting points are too low, which makes the heat of fusion too high; the logarithmic form of the equation exaggerates this error. We have attempted to measure the heats of fusion by the lowering of the melting point on addition of such substances as anthraquinone and benzil; but with the less fusible acids no definite readings could be obtained, owing to incipient decomposition. Where the corrections are for these reasons uncertain, the corrected values, which are undoubtedly too high, are enclosed in brackets. The values of the heats of fusion employed are given in Table III, those which are obtained by special cryoscopic experiments being marked with an asterisk. The value 4·83 for benzoic acid is taken from Ciamician and Garelli (*Zeitsch. physikal. Chem.*, 1895, **18**, 54); extrapolation of the Q-curves in benzene gave 4·5. From the former value we get at the triple point (95°) $p_{\text{liquid}}/p_{\text{solid}} = 1{\cdot}59$. The observed vapour pressure by steam distillation was 1·129 mm., so that the corrected value for the pure liquid at 100° would appear to be $1{\cdot}129 \times 1{\cdot}59 = 1{\cdot}79$ mm. Kahlbaum's measurements of the vapour pressure of the liquid acid (*Zeitsch. physikal. Chem.*, 1898, **26**, 603) (by a rather large extrapolation, his lowest value being 10 mm. at 132·5°) give 1·7 mm. at 100°.

TABLE V.

Acid.	Hydroxybenzoic acids.			Hydroxytoluic acids.				
	Ortho-.	Meta-.	Para-.	1 : 2 : 3-.	1 : 2 : 4-.	1 : 2 : 5-.	1 : 3 : 4-.	1 : 4 : 3-.
Vap. press. at 100°	Obs. 39·7	0·149	0·030	23·5	12·1	18·2	1·76	0·072
in mm. × 100 ...	Corr. 86·2	(25·7)	(2·48)	98·2	50·7	46·2	(15·1)	0·727
Critical solution temp. in water...	89·5°	v. low	v. low	153·5°	145·2°	142·8°	(+9°)	(+17°)
Increase of Q in benzene............	8·0	65·6	69·2	5·2	7·5	6·4	35·9	29·4
Increase of Q in heptane...........	43·8	∝	∝	29·2	31·3	45·0	∝	∝

Acid.	Nitrobenzoic acids.			Chlorobenzoic acids.			Benzoic acid.	Phenyl-acetic acid.	β-Phenyl-propionic acid.
	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.			
Vap. press at 100°	Obs. 2·01	0·70	0·096	18·0	19·7	4·59	112·9	29·6	22·5
in mm. × 100	Corr. 6·05	2·12	(0·592)	29·8	33·3	(94·0)	179	54·1	29·3
Critical solution temp. in water	52°	109·5°	118°	126°	143°	167°	116·2°	108·0°	150·0°
Increase of Q in benzene	25·3	8·8	24·9	5·4	7·3	4·4	3·0	2·9	1·4
Increase of Q in heptane	∝	∝	∝	79·6	23·8	18·4	—	—	—

The sign of infinity, ∝, indicates the existence of a stable two-liquid area.

The results are summarised in Table V, which shows (1) the vapour pressure of the acid in hundredths of a mm. at 100° (obtained by steam distillation, T., 1920, **117**, 396); (2) the critical solution temperature in water (values in brackets are calculated from the slope of the curve); (3) the increase of the heat of solution in benzene (difference between the maximum value and that for 95 molecules per cent., which is nearly the heat of fusion); (4) the corresponding increase in heptane.

Among the hydroxy-acids, which are typical abnormal compounds, it will be seen that the solubility relations are reversed as we pass from water to benzene; the isomerides with the lowest critical solution temperature (greatest solubility) in water show the largest increase in heat of solution (indicating the least solubility) in benzene. Heptane shows the same properties as benzene, but in a more marked degree. The isomerides with the greatest solubility in water invariably have the smallest vapour pressure. The alcohols occupy a peculiar position, the solubilities being abnormally high in every case, as is indicated by the fall in the Q values. Thus at 60° *o*-hydroxybenzoic acid is more than two hundred times as soluble (as measured by the molecular concentrations) in ethyl or butyl alcohol as in water, and more than twenty times as soluble in either as in benzene: with the para-acid, the solubility in the alcohols is thirty to fifty times as great as in water, and upwards of one thousand times as great as in benzene. Walker and Wood's measurements (T., 1898, **73**, 618) show that ether and acetone resemble the alcohols in this respect. In the neighbourhood of 20° the ortho-acid is about six hundred times as soluble in either as in water, and about forty times as soluble as in benzene: the para-acid about one hundred times as soluble as in water, and from three thousand to six thousand times as soluble as in benzene.

A possible explanation may be suggested for this remarkable difference. When a substance forms a compound with the solvent, its solubility is thereby increased, since in addition to the amount present in solution as such, there is the amount present as compound. Examples are quoted at the end of the following paper (for example, nitrophenols in aniline) where the formation of a compound (which can be isolated) determines a large increase in the solubility, and a corresponding fall in the heat of solution. It is therefore possible that these acids form compounds in solution with the alcohols, and these might perhaps be isolated if the solubility curves were carried to a low enough temperature. It must, however, be observed that the results of Pickering (T., 1893, **63**, 1023) with acetic acid in methyl, ethyl, and propyl alcohols do not support this view. He measured the solubility curve of the acid nearly to −80°, and obtained no definite evidence of the existence of a compound with the solvent, although the heats of fusion of the acid calculated from the results show the same diminution that we have observed, and the solubilities of the acid are correspondingly large.

A comparison of the solubilities of the three hydroxybenzoic acids in various solvents at moderate temperatures brings out the remarkable result that the ratio ortho : para, which is very small in water, rises as the dielectric constant of the solvent falls, reaching a maximum in benzene * which is yet far short of the ratio of the vapour pressures. The ratio meta : para, which is very much nearer to unity, tends to rise in the same direction. The values at and near 20° are taken from Walker and Wood.

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* The values in heptane have not been determined, but the ratio would obviously be larger still.

Solvent.	Water.		Ethyl alcohol.	Butyl alcohol.	Acetone.	Ether.	Benzene.		Vap. press.
	60°	20°	60°	60°	23°	17°	60°	20°	100°
Dielectric const.	80		25	19	21·5	4·3	2·3		1
Ortho/para	0·200	0·388	1·63	0·855	1·46	2·67	127·5	193·4	1320
Meta/para	0·739	1·84	1·03	0·560	1·17	1·03	1·04	2·76	4·53

The ortho-acids behave like non-hydroxylic ("non-polar") compounds, and are more soluble in non-associated solvents of low dielectric power, while the para-, and in a rather smaller degree the meta-, have the opposite character. The alcohols, ether, and acetone have an equally high solvent power for both classes.

The hydroxytoluic acids closely resemble the hydroxybenzoic, and give a good illustration of the difference between normal and abnormal behaviour. The three in which the hydroxyl- and carboxyl-groups are in the ortho-position to one another are almost identical in all these properties: vapour pressure, and solubility in water, benzene, and heptane. A change in the position of the methyl group is practically without effect. When, however, the hydroxyl group is shifted to the meta- (1 : 3 : 4-) or para- (1 : 4 : 3-) position with respect to the carboxyl, these properties are entirely altered.

Of the other groups of acids, the chloro-derivatives are practically normal; their vapour pressures and solubilities are of the same order. The nitro-acids are abnormal, but in a different sense from the hydroxy-acids. The differences in volatility are distinct, although not large; the ortho-compound, as usual, has the highest vapour pressure. But the solubilities, which are very different, are the reverse of what we should expect, the ortho-acid having the lowest and the para- the highest critical solution temperature in water; the meta-, as usual, resembles the para-. In benzene, the solubilities of the ortho- and meta-compounds are in the opposite order to those in water, as we should expect; but the para-compound, although the least soluble in water, is also about as insoluble in benzene as the ortho-. The unusual relation between the slope of the solubility curve and the critical solution temperature in benzene is another anomaly in this group. The nitrobenzoic acids are the only abnormal group hitherto examined which does not contain a phenolic hydroxyl group, and this may explain why this kind of anomaly has not been observed elsewhere.

The mono-substituted acids, benzoic, phenylacetic, and β-phenylpropionic, with their high vapour pressures, somewhat high critical solution temperatures in water, and low heats of solution in benzene, resemble rather the ortho- than the para-hydroxy-acids, as do also the three chloro-acids.

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CVIII.—*Influence of Position on the Solubility and Volatility of the Mono- and Di-nitrophenols.*

By Nevil Vincent Sidgwick and Wilfrid Major Aldous.

The mononitrophenols have been shown to be highly abnormal as regards their solubility in water, the ortho-compound being far less soluble than the other two. In the following paper, the solubilities of five of the six dinitrophenols in water and benzene are described, and also their volatility in steam, together with that of the mononitro-compounds and picric acid; and the interpretation of the results is discussed.

EXPERIMENTAL.

Preparation of Materials.

In indicating the structure of the isomerides, the hydroxyl group is always taken to occupy position 1.

o- and p-*Nitrophenol.*—Ordinary pure laboratory specimens were further purified by steam distillation and recrystallisation.

m-*Nitrophenol.*—This was made by the usual method of diazotising *m*-nitroaniline (Bantlin, *Ber.*, 1868, **11**, 2100; Holleman and Wilhelmy, *Rec. trav. chim.*, 1902, **21**, 432). Various efforts were made to diminish the bulk of the solution during the decomposition of the diazo-compound, while avoiding excessive resinification. The use of copper sulphate as a catalyst was found to be disadvantageous. The process finally adopted was as follows:

Fourteen grams of *m*-nitroaniline were dissolved in 200 c.c. of water containing 35 c.c. of concentrated sulphuric acid. The solution was filtered and cooled in ice, when the sulphate separated as a pink paste. The concentrated nitrite solution was added slowly with stirring, and the sulphate dissolved. The cold filtered solution was then added very slowly to a boiling solution of 40 c.c. of concentrated sulphuric acid in 500—600 c.c. of water and the solution boiled until nitrogen ceased to be evolved and the liquid became clear. It was then allowed to cool somewhat, in order to permit the resin to settle, filtered, cooled, and extracted with ether. The crude product, after evaporation of the ether, was recrystallised from hydrochloric acid (yield 9—10 grams). In this way, the bulk of the liquid is reduced to about a quarter of that used by Holleman and Wilhelmy for the same weight of *m*-nitroaniline.

Dinitrophenols : 1 : 2 : 4- and 1 : 2 : 6-.—Prepared by nitration of *o*-nitrophenol, and purified and separated as described by Holleman and Wilhelmy (*loc. cit.*).

Melting points : 1 : 2 : 4-, 112·9° ; 1 : 2 : 6-, 62·2°.

1 : 3 : 4-, 1 : 3 : 6-, and 1 : 3 : 2-.—These were all made by the nitration of *m*-nitrophenol, by the method described by Holleman and Wilhelmy, but this was modified in some respects.

The 1 : 3 : 6- is easily removed by making use of its relatively small solubility in cold alcohol; the other two can be separated by crystallisation from benzene. Holleman and Wilhelmy recommend that the benzene solution should be left overnight, but we find that in this case the 1 : 3 : 4- comes down contaminated with 1 : 3 : 2-, whereas if the benzene solution is rapidly cooled, and the crystals are filtered off at once, they are nearly pure. The method finally used was to dissolve the product from 20 grams of *m*-nitrophenol (after removing the 1 : 3 : 6- with alcohol, and drying) in 100 c.c. of benzene containing a little light petroleum (b. p. 60—80°). The solution was boiled for half an hour to let the resin collect, filtered, and cooled rapidly with stirring. The 1 : 3 : 4- (7 grams) which came out was filtered off at once, and the filtrate deposited during thirty-six hours 6 grams of 1 : 3 : 2-, mixed with some 1 : 3 : 4-. The 1 : 3 : 4- was recrystallised from benzene in the same way, and gave 4—5 grams of pure product, melting at 134·7° ; while the 1 : 3 : 2-, after two recrystallisations from hot water (with rapid cooling and immediate filtration), gave 3 grams, melting at 145·1°.

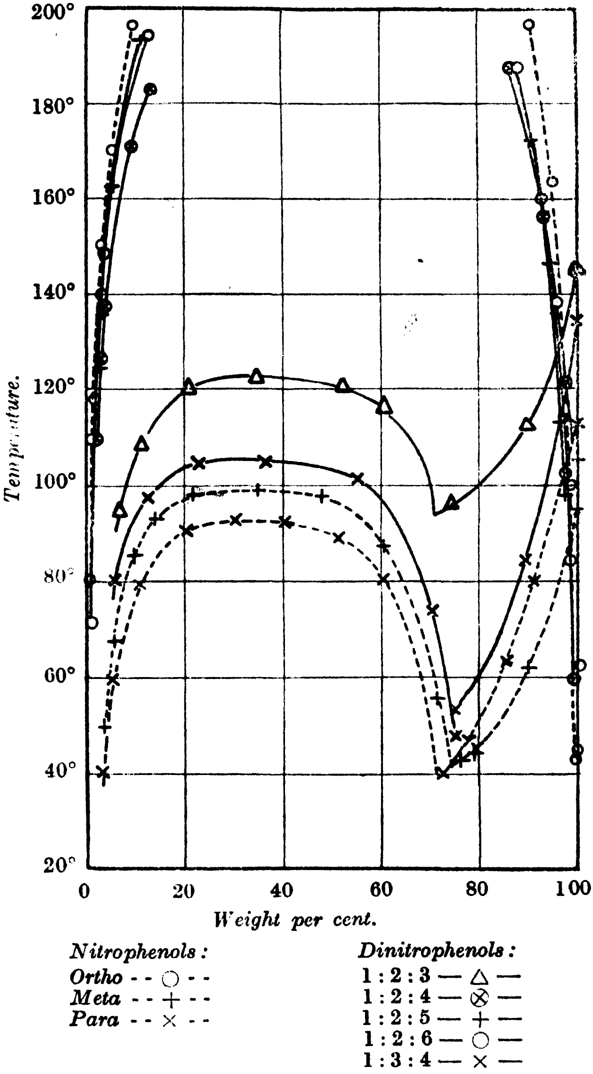
The benzene had been freed from thiophen by treatment with sulphuric acid, and frozen out seven times.

Determination of Solubilities.

These were carried out in the usual manner, by enclosing weighed quantities of the components in tubes, which were then sealed and the temperature determined at which the liquid separated into two layers, or the last crystals disappeared. The thermometer had been compared with a standard instrument, and the readings were corrected, when necessary, for the exposed stem.

Fig. 1.

Solubilities of nitrophenols and dinitrophenols in water.



The results are given in tables I and II, and plotted on Figs. 1 and 2. In Fig. 1 the solubilities of the three mononitrophenols in water are added (dotted lines) for comparison, the values being taken from Sidgwick, Spurrell, and Davies (T., 1915, **107**, 1202). The concentrations are expressed as grams of nitrophenol in 100 grams of solution. An asterisk indicates that the solid phase was present.

TABLE I.

Solubilities of Dinitrophenols in Water.

								1 : 3 : 4-.	
Sol^{y}.	Temp.	Sol^{y}.	Temp.	Sol^{y}.	Temp.	Sol^{y}.	Temp.	Sol^{y}.	Temp.
100·0	145·1°*	100·0	112·9°*	100·0	105·6°*	100·0	62·2°*	100·0	134·7°*
89·85	112·3*	99·02	108·1*	98·48	100·0*	99·11	59·5*	89·48	84·5*
74·32	96·0*	,,	100·5	97·50	98·0*	98·42	84·5	74·91	53·0*
60·44	116·7	98·24	117·6	,,	92·4	97·80	102·6	,,	48·0
52·15	120·4	97·70	121·7	96·72	113·5	95·96	138·3	70·23	73·8
35·13	122·2	97·14	131·2	94·51	146·4	93·44	158·0	55·40	101·6
20·83	120·1	93·35	156·0	91·73	172·2	—	—	36·65	105·2
10·90	108·2	86·36	187·7	—	—	12·26	192·5	23·28	104·6
6·74	94·5	—	—	12·24	194·5	3·97	147·9	12·79	97·5
		12·98	182·5	5·69	162·1	3·24	139·7	6·05	82·0
		8·99	170·5	3·91	146·4	1·87	117·6		
		3·81	137·7	2·97	135·8	1·00	89·5		
		2·98	126·1	2·33	124·7	0·703	71·1		
		1·95	109·6						
Crit. sol. temp.	122·5°		>200°		>200°		>200°		105·2°
Triple pt.	95·0		104·2		97·5		59·2		52·5°

TABLE II.

Solubilities in Benzene (Solid phase always present).

1 : 2 : 3-.		1 : 2 : 4-.		1 : 2 : 5-.		1 : 2 : 6-.		1 : 3 : 4-.	
Sol^{y}.	Temp.	Sol^{y}.	Temp.	Sol^{y}.	Temp.	Sol^{y}.	Temp.	Sol^{y}.	Temp.
100·0	145·1°	100·0	112·9°	100·0	105·6°	100·0	62·2°	100·0	134·7°
91·57	134·9	93·61	105·6	92·90	98·5	92·85	55·0	86·64	122·6
69·05	118·6	86·59	99·5	82·44	88·6	86·87	50·0	73·10	116·1
38·66	102·5	79·00	93·9	72·97	82·4	78·52	44·5	60·49	113·0
25·30	93·8	69·52	87·2	54·78	71·4	60·17	34·0	56·86	112·1
12·77	78·7	62·77	83·7	48·91	67·9	43·36	25·5	41·65	109·1
		52·36	77·1	33·81	57·0			27·27	106·5
		34·60	65·0	24·22	48·5			6·54	89·2
		21·01	51·0	13·96	33·5				

Measurement of the Heat of Fusion from the Freezing-point Constant.

These constants were determined in the usual Beckmann apparatus in a glycerine bath; benzil, *p*-dibromobenzene, and anthraquinone were used as solutes. Owing to the difficulty of inducing crystallisation in the nitrophenols, it was found necessary to cool until a considerable amount of solid had separated, and then to raise the temperature slowly until only a trace of crystals remained.

The 1 : 2 : 3-dinitrophenol, when fused, slowly darkened, and its melting point fell continuously, so that no results could be obtained.

The results are tabulated below, *E* being the cryoscopic constant, and *Q* the heat of fusion in kgr.-cals. per gram-molecule.

Dinitro-phenol.	Solute.	Per cent. Solute.	Deprⁿ.	*E*.	
1 : 2 : 4-	Benzil	0·255	0·120°	98·7	Mean *E* : 94·9
		1·523	0·662	91·0	$Q=5·73$
1 : 2 : 5-	Dibromobenzene	0·667	0·230	81·4	Mean *E* : 83·2
		1·610	0·580	85·0	$Q=6·29$
1 : 2 : 6-	,,	0·639	0·255	94·1	Mean *E* : 93·1
		0·769	0·300	92·1	$Q=4·41$
1 : 3 : 4-	Anthraquinone	1·296	0·655	105·2	Mean *E* : 100·4
		1·416	0·650	95·5	$Q=6·05$

Volatility in Steam.

These measurements were carried out in the apparatus and under the conditions already described by one of us (Sidgwick, T., 1920, **117**, 389). The distillate was analysed by the method of Knecht and Hibbert (*Ber.*, 1903, **36**, 1549), by reduction with titanous chloride,* the excess of which was estimated with iron alum, using potassium thiocyanate as indicator. The method was tested with solutions of nitrophenols of known strength, and found to give satisfactory results, the error not exceeding one or two per cent.

The composition of the distillate was found to become constant after about an hour's distillation : thus, with 1 : 2 : 3-dinitrophenol, four successive portions of distillate required respectively 20·48, 20·36, 20·48, and 20·17 c.c. of titanous chloride solution per 100 c.c.

The volatility was measured not only of the dinitrophenols but also of the mononitro-compounds and of picric acid. The compounds all liquefied under water at 100° except 1 : 2 : 4-dinitrophenol and picric acid. *m*- and *p*-Nitrophenol are completely miscible with water at 100°; with these compounds the percentage composition of the liquid in the distilling flask was determined, and is given in brackets in the column headed "solubility" in the table below. In this table the first column gives the elevation of the boiling point of the liquid; the second the weight per cent. of nitrophenol in the distillate; the third the pressure of nitrophenol in the vapour (in hundredths of a mm.); the fourth the solubility in water at 100°; the fifth the partition coefficient (concentration in vapour divided by concentration in liquid). The sixth and seventh give the relative values of the vapour pressure and the partition coefficient, those for *p*-nitrophenol being taken as unity.

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* *p*-Nitrophenol is remarkable for the extreme slowness with which it is reduced by titanous chloride.

Substance.		*dt.*	Wt. per cent. in dist.	V.p. in mm. × 100.	Sol^y.	Partition.	Relative v.p.	Relative Part^n.
Nitrophenol	*o*-	—	2·79	283·0	1·08	1570	160	6280
	m-	0·25°	0·0596	5·87	(47·7)	0·733	3·32	3·07
	p-	0·24	0·0180	1·77	(42·3)	0·250	1	1
Dinitrophenol	1 : 2 : 3-	0·12	0·0736	5·48	7·8	5·6	3·10	22
	1 : 2 : 4-*	—	0·306	22·8	1·5	120	12·9	480
	1 : 2 : 5-	0·06	0·599	44·8	1·4	250	25·3	1010
	1 : 2 : 6-	—	0·147	11·0	1·3	67	6·20	270
	1 : 3 : 4-	0·34	0·00139	0·103	15	0·054	0·0582	0·218
Picric acid *		0·40	0·00417	0·249	6·33	0·388	0·441	1·55

* Solid under water at 100°.

Corrected Vapour Pressures for Pure Liquids.

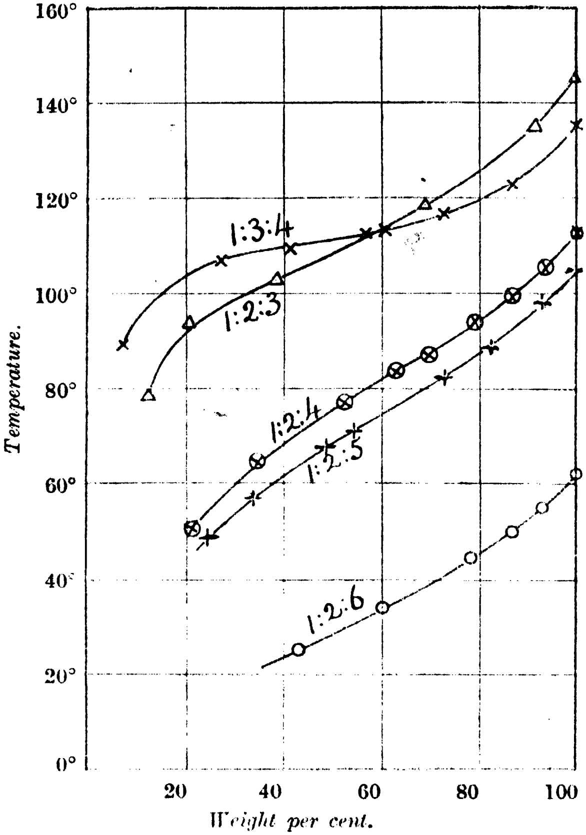
From these values we can calculate the vapour pressures of the pure liquids by the methods described in the preceding paper, the ratio of the vapour pressures of liquid and solid being given by the equation

$$2{\cdot}3026 \log \frac{p}{p^1} = \frac{1000W}{R} \times \left(\frac{1}{T} - \frac{1}{T_0}\right).$$

When the substance is solid during the distillation, the value of this ratio at 100° is taken as the correction factor; when it is liquid, the value at the triple point. The heats of fusion employed are the following: for *o*-nitrophenol, 4·295 (Bogojawlenski, *Chem. Centr.*, 1905, II, 945; *Schriften d. Dorpater Naturfor. Ges.*, 1904, **13**, 1); the value of 3·72 given by Brunner (*Ber.*, 1894, **27**, 2102) is undoubtedly too low; for *m*- and *p*-nitrophenol, the values obtained by extrapolation from the heats of solution (see below) in toluene (Sidgwick, Spurrell, and Davies, *loc. cit.*) and in trichloroacetic acid (Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 1309), which agree well with one another; for 1 : 2 : 3-dinitrophenol, the extrapolated value from the heats of solution in benzene; for the other four dinitrophenols, those obtained from the cryoscopic experiments already described. These values are given in Table III (p. 1010). For picric acid there are no satisfactory data; but since the heat of fusion of *o*-nitrophenol is 4·30, of 1 : 2 : 4-dinitrophenol 5·73, and of the 1 : 2 : 6-isomeride 4·71, we may probably assume without serious error (as the correction is only small) that the heat of fusion of picric acid is 5; and the correction has been calculated on this basis. A difficulty arises with *m*- and *p*-nitrophenol from the fact that they are miscible with water in all proportions at 100°, so that the solutions distilled were necessarily unsaturated, and their vapour pressure correspondingly lowered. It is impossible to make any definite allowance for this; but owing to the flatness of the vapour-pressure curves in the neighbourhood of the two-liquid area (which is in both cases within 10° of the point of observation), the error is not likely to be large. The corrected values of the vapour pressures are given in the table on p. 1009.

FIG. 2.

Solubilities of dinitrophenols in benzene.



Discussion of Results.

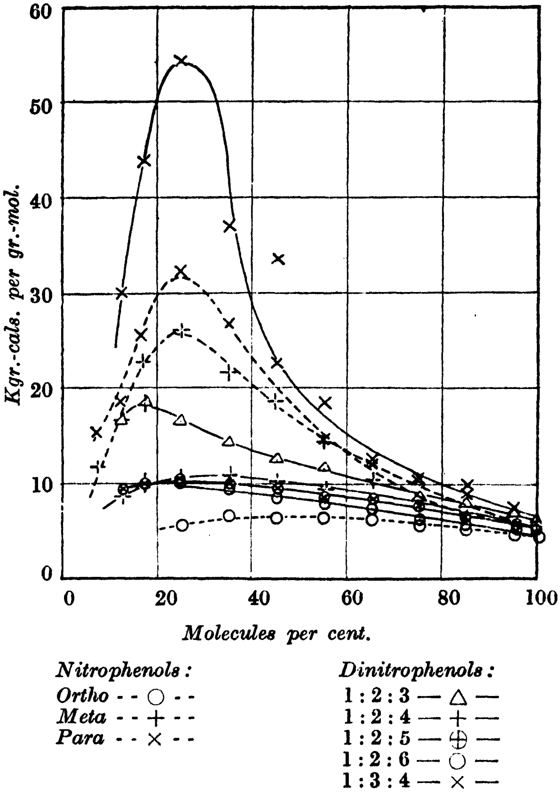
Solubilities in Water.

The curves (Fig. 1) show a marked similarity to those of the mononitrophenols, which are given in dotted lines on the diagram.

The behaviour of *o*-nitrophenol is closely followed by that of the 1 : 2 : 4-, 1 : 2 : 5-, and 1 : 2 : 6-dinitro-compounds. In all these the solubilities are very small, and the critical solution temperature is somewhere above 200°. On the other hand, the *m*- and *p*-nitrophenol curves resemble that of the 1 : 3 : 4-dinitrophenol, the only isomeride examined in which no ortho-position is occupied. That is, the influence of the ortho-nitro-group in diminishing the solubility prevails, and to nearly the same extent, whether the second nitro-group is in positions 4, 5, or 6; whereas if there is no ortho-nitro-group, the solubility is much greater. A remarkable anomaly is offered by the 1 : 2 : 3-compound. Although the ortho-meta-derivative which has the two nitro-groups on opposite sides of the ring (1 : 2 : 5) is scarcely more soluble than the di-ortho- or the

FIG. 3.

Nominal heats of solution of mono- and di-nitrophenols in benzene.



ortho-para-, the other ortho-meta-derivative (1 : 2 : 3), in which they are on the same side, is nearly as soluble in water as the meta-para-isomeride. This anomaly is repeated in the volatility and in the heat of solution in benzene. The peculiarity is so far unexplained. We do not even know whether it depends on the chemical nature of the adjacent group, or merely on its steric effect. This can only be determined by examining such compounds as the nitrocresols. It is to be noticed that the hydroxytoluic acid ($CO_2H : OH : CH_3 = 1 : 2 : 3$) (see preceding paper) shows no corresponding anomaly; it in no way differs from the other isomerides in which the carboxyl and hydroxyl groups are next to one another.

Nominal Heats of Solution.

The nominal heats of solution in benzene have been calculated by the methods described in the preceding paper. The values for the mononitrophenols have been added, from the solubility data of Bogojawlenski, Boguljubow and Winogradow (*Chem. Centr.*, 1907, I, 1738; *Schriften d. Dorpater Naturfor. Ges.*, 1907, **15**, 216). The results are given in Table III and Fig. 3, the heats being expressed in kgr.-cals. per gram-mol. The general results for all these compounds are briefly summarised in the following table, which gives the vapour pressure at 100° (observed and corrected), the critical solution temperatures in water, and the increase of the heat of solution in benzene.

	Nitrophenols.			Dinitrophenols.					
Compound.	Ortho-.	Meta-.	Para-.	1 : 2 : 3-.	1 : 2 : 4-.	1 : 2 : 5-.	1 : 2 : 6-.	1 : 3 : 4-.	Picric Acid.
Vap. press. at 100° in mm.×100...	Obs. 283	5·87	1·77	5·48	22·8	44·8	11·0	0·103	0·249
	Corr. 292	19·6	8·28	12·8	29·4	50·6	11·7	0·664	0·364
Crit. sol. temp. in water	v. high	— 98·7°	92·8°	122·5°	v. high	v. high	v. high	105·2°	
Increase of *Q* in benzene	2·2	18·7	26·4	12·1	4·9	4·0	5·1	46·4	

It will be seen that in each group the three properties—a high vapour pressure, a small solubility (high critical solution temperature) in water, and a large solubility (small rise in *Q*) in benzene—go together. *o*-Nitrophenol and, with one marked exception, all the dinitrophenols which have at least one ortho-position occupied have these characteristics, and the occupation of a second ortho-position does not greatly increase them, whilst those compounds (*m*- and *p*-nitrophenol, and 1 : 3 : 4-dinitrophenol) in which neither ortho-position is occupied have low vapour pressures, are much more soluble in water, and show a much larger increase of the heat of solution in benzene. The one exception, the anomalous 1 : 2 : 3-dinitrophenol, is intermediate in all these properties between these two groups.

TABLE III.

Nominal Heats of Solution in Benzene (Molecular, in kgr.-cals.).

Mean mol. per cent.	Mononitrophenols. Ortho-.	Meta-.	Para-.
95	4·56	7·82	5·73
85	5·17	8·86	6·70
75	5·44	9·85	8·82
65	6·09	12·20	10·20
55	6·29	14·63	14·69
45	6·30	18·62	22·45
35	6·75	21·60	26·46
25	5·68	26·54	32·10
17·5	—	22·92	25·58
12·5	—	16·62	18·62
7·5	—	12·90	15·81
Mol. heat of fusion	4·295	5·20	5·05

Mean mol. per cent.	Dinitrophenols. 1 : 2 : 3-	1 : 2 : 4-.	1 : 2 : 5-.	1 : 2 : 6-.	1 : 3 : 4-.
95	6·19	6·09	6·36	5·08	7·54
85	7·90	6·88	6·91	5·64	9·24
75	—	7·66	7·47	6·22	10·26
65	10·09	8·73	8·41	7·40	12·52
55	11·40	9·64	8·76	8·04	18·44
45	12·59	10·23	9·66	8·58	33·42
35	14·18	10·98	10·39	9·54	37·04
27·5		—	—	10·00	—
25	16·56	10·82	10·39	-	53·94
17·5	18·33	10·54	10·42	—	43·71
12·5	16·78	8·77	9·59	—	30·33
Mol. heat of fusion	5·20	5·70	6·29	4·41	6·05

The solubilities of mononitrophenols have been measured in various other solvents: in aniline, urea, and picric acid (Kremann and Rodinis, *Sitzungsber. K. Akad. Wien*, 1905, **117**, 1237), in naphthalene (Kremann, *ibid.*, 1904, **116**, 865), in toluene, bromobenzene, and ethylene dibromide (Sidgwick, Spurrell, and Davies, *loc. cit.*), and in trichloroacetic acid (Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 1309); in some of these solvents the meta-compound was not examined. The solubility of 1 : 2 : 4-dinitrophenol has been measured by Kremann in aniline (*Sitzungsber. K. Akad. Wien*, 1906, **118**, 427) and in naphthalene (*ibid.*, 1904, **116**, 865), and by Kremann and Hofmeier in phenanthrene (*ibid.*, 1910, **122**, 121). We have calculated the heats of solution in all solvents in which the curve could be carried far enough. The increase in the heat is:

Solvent.	Toluene.	Naphthalene.	Bromobenzene.	Ethylene dibromide.	Trichloroacetic acid.	Aniline.	Phenanthrene.
Ortho-	2·9	(0·8)	1·4	(1·0)	0·2	0·4	—
Meta-	39·4	—	—	—	0·1	−3·0	—
Para-	32·1	8·6	20·3	11·6	0·0	−2·4	—
1 : 2 : 4		(0·2)	—	—	—	−1·9	−1·3

(Where the values are in brackets, the solubilities do not extend beyond 75 molecules per cent.).

Toluene, bromobenzene, and ethylene dibromide are very similar to benzene in their solvent action. Trichloroacetic acid is remarkable for the extraordinary constancy of the heat values, which are practically unaffected by concentration with any of the three isomerides. In aniline, *o*-nitrophenol gives constant values, whilst those of the *m*- and *p*-nitrophenols fall rapidly, the solubility being abnormally high. This is no doubt connected with the fact that these two form stable compounds with aniline, which the ortho-derivative does not. A similar fall in the *Q* values occurs with 1 : 2 : 4-dinitrophenol in phenanthrene, where again a compound is formed. An analogous fall, which may be due to the same cause, was observed in the heat of solution of the hydroxybenzoic acids in ethyl and butyl alcohols.

It is known that the chlorophenols show differences in vapour pressure (as indicated by the boiling points) comparable with those of the nitrophenols. In order to discover whether this abnormality extended to the solubility in water, some measurements were made with *o*- and *p*-chlorophenol in water. It was found that their critical solution temperatures differ widely (although not so much as those of the nitrophenols), and in the usual direction. The values are :

Position.	Ortho-.	Meta-.	Para-.
Boiling point	175°	214°	217°
Crit. sol. temp. in water	186°	—	125°

This is exactly parallel to the behaviour of the nitrophenols; the ortho-compound has by far the lowest vapour pressure, the para- the highest, and the meta- comes very near the para-; and the ortho- is much less soluble in water than the para-. This is of some interest, since it has been shown that the introduction of a chlorine atom into benzoic acid does not lead to any serious abnormality of behaviour.

In view of the possible suggestion that these abnormalities are due to association, the experiments of Hewitt and Winmill on the surface tensions of the substituted phenols (T., 1907, **91**, 441) are of interest. They calculated from their results the following values of the association factor; the figures in brackets after each value give the temperature range over which the measurements were taken :

	Ortho-.	Meta-.	Para-.
Cresols...............	1·12 (40–67°)	1·48 (19–57°)	1·62 (46–74°)
	1·06 (67–100°)	1·33 (57–100°)	1·26 (74–100°)
Nitrophenols	0·84 (53–79°)	1·48 (116–147°)	1·25 (130–163°)
Chlorophenols ...	1·0 (13–45°)	1·49 (33–79°)	1·22 (52–72°)
	1·0 (45–73°)	1·11 (78–139°)	1·08 (72–100°)

It will be seen that the cresols, which in our sense are quite normal give as much indication of association in the meta- and para-compounds as the nitrophenols, and much more than the chlorophenols; and the degree of association (which practically never reaches 50 per cent.) seems quite insufficient to account for the enormous difference in solubility and vapour pressure.

There is an obvious connexion between our results and those of Auwers (*Zeitsch. physikal. Chem.*, 1893, **12**, 689; 1895, **18**, 599; 1897, **23**, 449; 1899, **30**, 300; Auwers and Orton, *ibid.*, 1896, **21**, 337) on the depression of the freezing point of solvents such as benzene or naphthalene by isomeric aromatic derivatives. Speaking generally, Auwers finds that among what we have called abnormal groups the ortho-compound gives a normal lowering of the freezing point, whilst with the meta- and para- the lowering is less than we should expect. This is commonly expressed by saying that the molecular weights (calculated on the usual formula) for the ortho-compounds are normal, while the isomerides are associated. We might, however, equally well say that if we assume the molecular weights of the solute in the latter case to be normal, the calculated heats of solution of the solvent are abnormally high. So in our experiments, when on our assumption of normal molecular weights the heats of solution are high, we might have taken the heats to be normal, in which case the molecular weight of the benzene would have been calculated to be very high. The two results are really parts of the same phenomenon. The lowering of the freezing point is a measure of the fall of the partial pressure of the component which freezes out. In such a system as, say, benzene and *p*-nitrophenol, our results show that the vapour pressure of the nitrophenol is less lowered by the addition of benzene than the mixture law requires. Auwer's results show that this is true also of the effect of the solute on the vapour pressure of the benzene. Both results are necessary in a system which is near the temperature at which it separates into two layers. In such cases the isothermal vapour-pressure curve has the same general form for each component: starting from the pure component, it falls less rapidly than we should expect, becomes nearly flat (horizontal if separation occurs) towards the centre of the diagram, and then falls very steeply towards the end. The relation is symmetrical with respect to the two components, and cannot be taken by itself as evidence that the nitrophenol is associated, any more than that the benzene is associated. What it does show is that the two liquids are not far removed from the temperature of imperfect miscibility.

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CIX.—*The Solubility and Volatility of the Chloro- and Nitro-anilines and of their Acetyl Derivatives.*

By Nevil Vincent Sidgwick and Howard Ernest Rubie.

The nitrophenols and the nitrobenzoic acids are abnormal compounds in the sense that their solubility and volatility are greatly affected by the orientation. The chlorophenols are also undoubtedly abnormal, to judge by the difference in their boiling points and solubility in water, while the chlorobenzoic acids are practically normal. In the following investigation, the behaviour is examined from this point of view of the corresponding chloro- and nitro-derivatives of aniline and acetanilide.

EXPERIMENTAL.

Preparation of Materials.

Chloroanilines.—*o*- and *p*-Chloroaniline were made by reduction with iron of the corresponding chloronitrobenzenes (recrystallised, melting at 32·0° and 82·0° respectively). The ortho-compound was freed from traces of the para- by dissolving in an equivalent of sulphuric acid and distilling with steam, when the ortho- alone came over (Beilstein and Kurbatoff, *Annalen*, 1875, **176**, 27). It was colourless, distilled at 207·0°, and solidified at —2·1°. These values agree with those of Rinkes (*Rec. trav. chim.*, 1911, **30**, 79). The para-compound after recrystallisation from light petroleum melted sharply at 70·5° (Rinkes, *loc. cit.*; Lobry de Bruyn, *ibid.*, 1916, **36**, 153).

m-Chloroaniline was prepared from *m*-chloronitrobenzene, which was made by the chlorination of nitrobenzene at 100° in presence of 5 per cent. of antimony trichloride, care being taken to exclude moisture (Varnholt, *J. pr. Chem.*, 1887, [ii], **36**, 29). The nitro-compound melted after recrystallisation at 43·1° (agreeing with Rinkes, *loc. cit.*), and on reduction with iron filings gave a 90 per cent. yield of *m*-chloroaniline, which distilled constantly at 118·5°/21 mm. and 230·5°/760 mm. It melted at —10·4° (—10·2°, Lobry de Bruyn, *loc. cit.*).

The chloroacetanilides were made from these amines by heating them with 50 per cent. excess of glacial acetic acid, the water formed being allowed to distil off through the reverse condenser; in this way, the acylation is complete in one and a half hours. They were recrystallised from dilute acetic acid and then from aqueous alcohol.

Melting Points: Ortho-, 86·7°; meta-, 76·6°; para-, 178·4°. (Lobry de Bruyn gives 86·7°; 76·8°; 178·2°.)

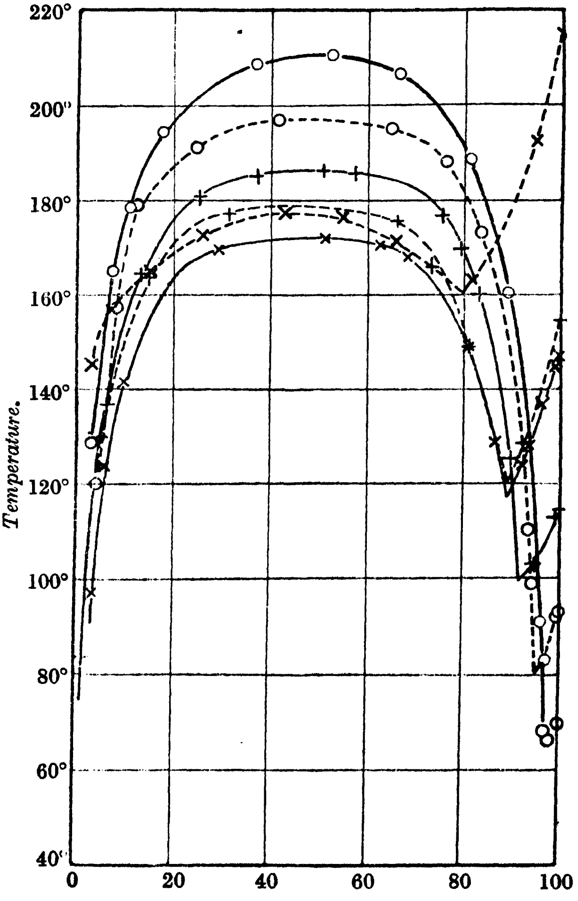
Nitroanilines and Nitroacetanilides.—*o*- and *p*-Nitroacetanilides

FIG. 1.

Solubility of nitroanilines and nitroacetanilides in water.

Full curves —— *Nitroanilines.*
Dotted curves - - - *Nitroacetanilides.*

Ortho — ○ —
Meta — + —
Para — × —

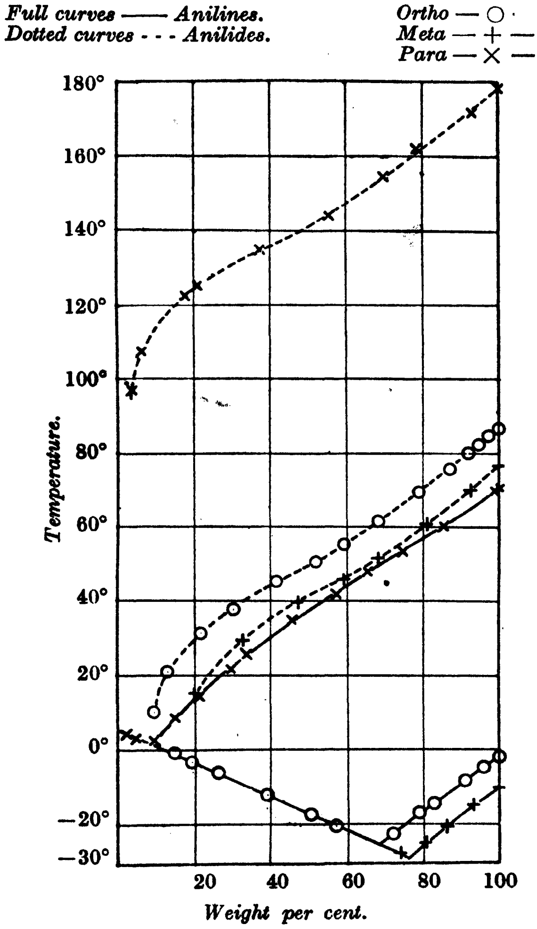


were made by the nitration of acetanilide, and separated by the difference of their solubilities in water. The para-compound melted after recrystallisation from 50 per cent. alcohol at 215·9°. This is considerably higher than the value (207°) given in the literature;

the compound may be dimorphic, like *p*-chloroacetanilide. *o*-Nitroacetanilide, obtained by concentrating the aqueous filtrate, melted after four recrystallisations from aqueous alcohol at 93·0° (the temperature given by Böeseken, *Rec. trav. chim.*, 1912, **31**, 350).

FIG. 2.

Solubility of chloroanilines and chloroacetanilides in benzene.

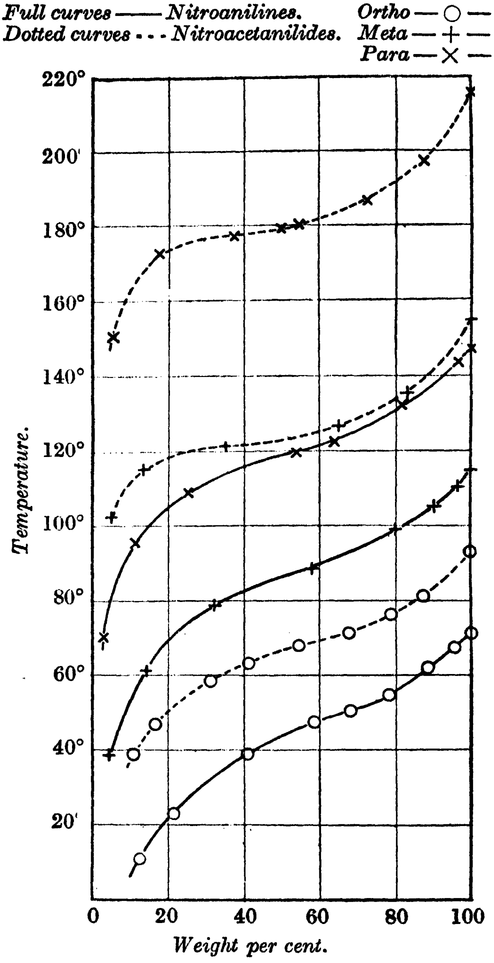


It was also prepared from the amine by acetylation, the method of Kaufmann (*Ber.*, 1909, **42**, 3480) of adding acetic anhydride to the benzene solution being found very satisfactory. *o*- and *p*-Nitroanilines were made by hydrolysing the acetyl compounds, and after recrystallisation from water the ortho- melted at 69·7° and the para- at 147·0°.

m-Nitroaniline, made by the reduction of *m*-dinitrobenzene, was three times recrystallised from water, and melted at 114·6°. Its acetyl derivative (recrystallised from dilute alcohol) melted at 154·5°.

FIG. 3.

Solubility of nitroanilines and nitroacetanilides in benzene.



Measurement of Solubilities.

These were carried out synthetically. At higher temperatures, sealed bulbs of 2 or 3 c.c. capacity were used; at lower, the observations were made in a Beckmann apparatus, one component being added from a weight-pipette.

The thermometers used had all been compared with a standard; the benzene had been freed from thiophen, and purified by repeated freezing out.

The results are given in the following tables, the concentration being expressed in grams of amine in 100 grams of solution.

Those points where the solid phase separated are marked in the water tables with an asterisk; with benzene, the solid phase was always present.

The solubilities of the chloro-derivatives in water are so small that they have not been plotted, but the others are given in Figs. 1—3.

TABLE I.

Solubilities of the Chloroanilines and Chloroacetanilides in Water.

Chloroanilines.						Chloroacetanilides.					
Ortho-.		Meta-.		Para-.		Ortho-.		Meta-.		Para-.	
Concn.	Temp.	Concn.	Temp.	Concn.	Temp.	Concn.	Temp.	Concn.	Temp.	Concn.	Temp.
100·0	− 2·1°	100·0	−10·4°	100·0	70·5°*	100·0	86·7°*	100·0	76·6°*	100·0	178·4°*
99·44	+19·0	99·51	− 6·0	99·11	69·0*	98·9	82·0*	98·00	69*	97·38	168*
98·50	75	98·85	+36	98·41	67·0*	97·43	77*	96·82	64*	93·16	150*
97·58	115	97·90	88	96·75	88	94·95	73*	94·41	81	89·60	142
96·02	155	96·50	130	96·27	100	92·87	105	91·29	123	88·08	160
—	—	—	—	94·28	145	88·72	150	86·86	165	85·23	178
3·35	158	2·23	150	—	—	85·12	175	—	—	—	—
2·19	130	1·47	125	4·62	160	—	—	6·14	176	3·85	169
1·25	95	0·91	100	3·26	136	10·71	182	2·76	138	1·87	140*
1·04	80	0·574	75	2·20	111	6·63	155	2·49	130	0·837	115*
0·916	71			1·04	55*	5·13	142	0·743	76	0·452	102*
				0·525	42*	2·94	105			0·384	97*
						1·69	85			0·095	65·5*
						0·692	65*				
						0·323	15*				

Composition and temperature at the triple point :—

99·8 per cent. −7·0°	99·5 −15°	97·5 +65°	95·0 70·0°	95·0 59·5°	90·0 138·0°

TABLE II.

Solubilities of the Nitroanilines and Nitroacetanilides in Water.

Nitroanilines.						Nitroacetanilides.					
Ortho-.		Meta-.		Para-.		Ortho-.		Meta-.		Para-.	
Concn.	Temp.	Concn.	Temp.	Concn.	Temp.	Concn.	Temp.	Concn.	Temp.	Concn.	Temp.
100·0	69·7°*	100·0	114·6°*	100·0	147·0°*	100·0	93·4°*	100·0	154·5°*	100·0	215·9°*
99·43	68·0*	99·86	113·5*	98·96	144·8*	99·38	92·4*	93·57	129·2*	95·20	192·2*
98·29	66·0*	94·96	103·2*	96·38	136·8*	97·11	83·2*	91·72	124·2*	81·84	163·6*
97·23	68·0	90·02	125·6	93·86	128·0*	94·54	99·0	81·18	149·2	65·84	171·7
96·16	91·0	83·60	159·9	92·52	124·2	93·65	110·2	73·74	166·4	54·93	176·6
92·06	142·0	79·82	169·3	86·82	129·2	83·47	173·1	66·08	175·7	42·65	177·4
89·50	160·2	75·77	176·7	81·27	148·6	76·28	188·0	31·13	176·9	25·62	172·8
81·88	188·5	57·55	185·8	68·19	167·8	65·04	195·0	14·52	163·5	14·36	164·2
66·89	206·2	50·57	186·1	62·58	170·4	41·16	197·0	5·21	130·0	7·08	156·5*
52·30	210·3	36·94	185·2	51·07	172·0	24·06	191·2			2·94	145·1*
36·71	208·6	25·39	180·5	39·49	172·0	11·97	179·2				
17·50	194·2	13·08	164·2	28·82	169·5	8·04	157·6				
10·74	178·5	6·04	136·5	9·29	141·5	3·97	120·0				
7·19	164·5	1·70	83·4*	5·16	123·5						
2·95	128·4			2·79	97·0*						

Critical solution temperatures :—

211·0°	187·5°	172·5°	198·0°	180·0°	178·0°

Composition and temperature at the triple point :—

97·5 per cent.	93·5	90·0	96·0	90·0	80·0
63·0°	99·0°	115·5°	81·0°	118·5°	161·5°

TABLE III.

Solubilities in Benzene. Solid Phase always present.

Chloroanilines.						Chloroacetanilides.					
Ortho-.		Meta-.		Para-.		Ortho-.		Meta-.		Para-.	
Concn.	Temp.	Concn.	Temp.	Concn.	Temp.	Concn.	Temp.	Concn.	Temp.	Concn.	Temp.
100·0	− 2·1°	100·0	−10·4°	100·0	+70·5°	100·0	86·7°	100·0	76·6°	100·0	178·4°
96·09	− 5·0	93·48	−15·5	98·90	70·0	97·45	84·8	92·74	70·0	93·62	172·0
91·19	− 8·7	86·18	−21·0	85·24	60·0	95·19	82·4	81·20	61·0	78·50	162·0
83·13	−14·4	80·82	−25·0	74·46	53·5	92·16	80·0	68·17	51·5	69·67	154·5
72·63	−23·0	64·33	−24·4 *b*	65·36	47·8	87·63	75·9	59·51	46·0	55·86	144·2
57·26	−21·0 *b*	47·02	−16·2 *b*	55·42	42·0	79·53	69·5	47·31	39·5	37·80	134·5
50·86	−17·4 *b*	43·28	−14·0 *b*	45·47	34·8	68·22	61·4	32·81	29·2	21·14	125·2
39·50	−12·0 *b*	35·48	−10·5 *b*	33·93	25·7	59·40	55·2	20·04	15·4	18·16	122·4
26·46	− 6·2 *b*	22·68	− 5·0 *b*	29·48	21·5	52·06	50·5			6·63	107·5
14·94	− 0·8 *b*	12·97	− 0·4 *b*	21·29	14·0	41·69	45·2			4·21	96·5
8·72	+ 1·5 *b*	7·20	+ 2·0 *b*	15·43	8·5	30·65	37·8				
0·00	+ 5·5 *b*	0·00	+ 5·5 *b*	9·42	2·4	21·77	31·4				
				4·66	3·4 *b*	13·50	20·2				
				2·87	4·2 *b*	9·56	10·0				
				0·727	5·1 *b*						
				0·00	5·5 *b*						

Eutectic composition and temperature :—

Ortho-.	Meta-.	Para-.
68·5 per cent.	75·5	8·5
−25°	−29·0°	+1·5°

The points marked *b* are those at which solid benzene separates.

TABLE IV.

Solubilities in Benzene.

Nitroanilines.

Ortho-.		Meta-.		Para-.	
Concn.	Temp.	Concn.	Temp.	Concn.	Temp.
100·0	71·1°	100·0	114·6°	100·0	147·0°
95·35	67·2	96·37	110·3	96·78	143·7
88·69	62·0	90·55	105·4	81·71	132·3
78·64	55·0	79·96	99·2	64·03	122·5
68·26	50·2	57·95	88·7	54·15	119·5
58·96	47·4	32·42	78·4	25·46	108·6
40·92	39·2	14·18	60·9	11·42	95·0
21·52	23·2	4·42	38·2	3·21	70·0
12·26	10·5				

Nitroacetanilides.

Ortho-.		Meta-.		Para-.	
Concn.	Temp.	Concn.	Temp.	Concn.	Temp.
100·0	93·0°	100·0	154·5°	100·0	215·9°
87·58	81·2	83·07	135·3	87·48	197·4
79·08	76·4	65·27	126·8	72·62	186·5
67·97	71·5	35·13	121·2	54·78	180·3
54·97	68·0	13·47	115·0	49·93	179·4
41·62	63·2	5·04	102·0	37·75	177·5
31·49	58·5			17·47	172·6
16·44	46·8			5·23	150·6
10·26	39·0				

Determination of Heats of Fusion.

These were determined by measuring the depression of the freezing point of the amine by benzene, dibromobenzene, or benzil in a Beckmann apparatus. The results (expressed in kgr.-cals. per gram-molecule) are given in the following table. The values obtained by extrapolation from the heat of solution (Q)-curves in benzene (which are, of course, less trustworthy) are added for comparison; the agreement is on the whole good.

	Chloroaniline.			Chloroacetanilide.		
Substance.	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.
Direct	2·84	2·78	4·80*	6·04	4·32	9·74
From Q-curve	2·8	2·6	5·1	6·1	4·5	9·4

	Nitroaniline.			Nitroacetanilide.		
Substance.	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.
Direct	3·70	4·16	5·68	5·41	3·24	4·44
From Q-curve	3·9	4·5	5·9	4·7	3·3	4·4

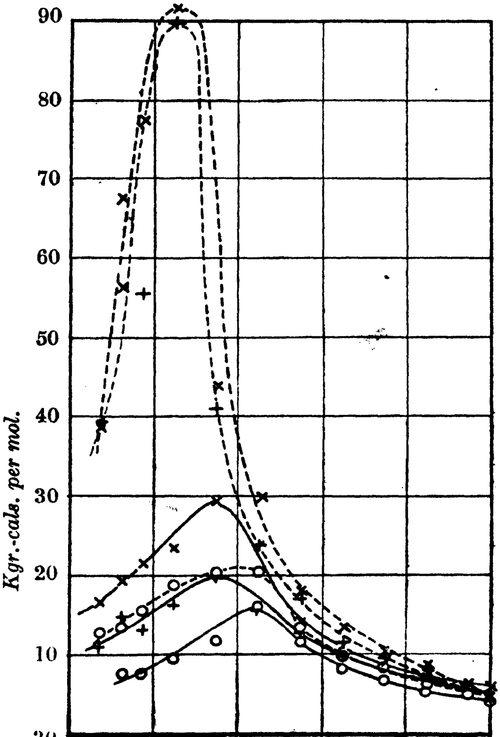
---

* Bruner (*Ber.*, 1894, **27**, 2102) determined this calorimetrically and obtained the value 4·724.

FIG. 5.

Heats of solution of nitroanilines and nitroacetanilides in benzene.

Full curves —— *Nitroanilines.* *Ortho* — ○ —
Dotted curves - - - *Nitroacetanilides.* *Meta* — + —
Para — × —



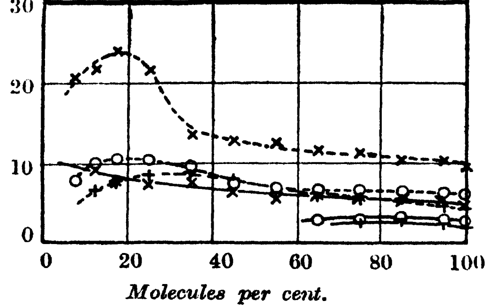


FIG. 4.

Heats of solution of chloroanilines and chloroacetanilides in benzene.

Full curves —— *Chloroanilines.* *Ortho* — ○ —
Dotted curves - - - *Chloroacetanilides.* *Meta* — + —
Para — × —

Volatility in Steam.

This was measured in the apparatus already described. The chloroanilines were estimated in the distillate by titration at about −10° with *N*/10-potassium nitrite, using starch-iodide as indicator. The chloroacetanilides were treated in the same way, after previous hydrolysis by boiling for three hours with concentrated hydrochloric acid. The nitroanilines and nitroacetanilides were determined by reduction, by boiling for fifteen minutes with excess of titanous chloride, and estimating the excess with iron alum. Where necessary, alcohol was added to dissolve the organic compound, and in these cases the small amount of reducing solution used up by the quantity of alcohol employed was determined, and the necessary correction applied. These methods of analysis were tested with known amounts of the amines in every case, and found satisfactory.

From these results the corrected vapour pressures for the pure liquids at 100° were calculated by the methods described in the two preceding papers, the correction factor for the triple point being used when the amine is liquid at 100°. The heats of fusion used were those obtained from the cryoscopic experiments described above. The vapour-pressure curves of *o*- and *m*-chloroaniline have been measured by Kahlbaum (*Zeitsch. physikal. Chem.*, 1898, **26**, 627), and the values for 100°, interpolated from his measurements, are given in brackets in the table. In both cases our corrected values are almost exactly 4 per cent. smaller than his. Table VI gives the observed and corrected vapour pressures.

Nominal Heats of Solution.

These values have been calculated from the solubility curves in benzene for every successive 10 (molecular) per cent., by means of the formula

$$\log_e \frac{s}{s_1} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right).$$

The results are given in Table V, and plotted on Figs. 4 and 5.

Discussion of Results.

The properties of these compounds are summarised in Table VI, which gives (1) the vapour pressures at 100° (observed and corrected), (2) the critical solution temperatures in water (when these can be determined), and (3) the increase of the heat of solution in benzene (the difference between its maximum value and the heat of fusion).

It is evident that the chloroanilines are a normal group of isomerides. Their vapour pressures do not differ to any marked

TABLE V.

Nominal Heats of Solution in Benzene.

(Kgr.-cals. per gram-molecule.)

Mean mol. per cent.	Chloroanilines.			Chloroacetanilides.		
	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.
95	3·01	2·83	5·29	6·33	4·84	10·2
85	3·31	3·04	5·63	6·40	6·24	10·2
75	3·05	2·80	5·96	6·71	6·32	11·1
65	2·95	—	6·55	6·82	6·94	11·5
55	—	—	6·80	7·00	6·75	12·4
45	—	—	6·48	7·26	7·93	12·8
35	—	—	7·06	9·73	9·36	13·6
25	—	—	7·22	10·4	8·61	21·5
17·5	—	—	7·82	10·5	7·95	24·0
12·5	—	—	9·32	10·0	6·62	21·8
7·5	—	—	—	7·92	—	20·7
Heat of fusion	2·84	2·78	4·80	6·04	4·32	9·74

Mean mol. per cent.	Nitroanilines.			Nitroacetanilides.		
	Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.
95	4·38	5·24	6·50	5·12	4·75	5·51
85	5·11	6·59	7·62	6·26	7·25	7·69
75	6·69	8·86	8·60	8·54	9·36	10·3
65	8·11	9·54	10·8	9·90	11·28	13·2
55	11·0	12·8	13·9	13·2	16·8	17·8
45	15·9	15·3	23·7	20·2	23·6	29·8
35	11·5	19·8	29·1	20·1	40·9	43·6
25	9·41	16·0	23·2	17·6	89·8	96·5
17·5	7·39	12·8	21·4	15·4	55·4	77·1
12·5	7·79	14·8	19·1	13·4	56·2	67·3
7·5	—	10·9	16·3	12·9	39·1	38·6
Heat of fusion	3·70	4·16	5·68	5·42	3·24	4·44

TABLE VI.

Compound.		Chloroanilines.			Chloroacetanilides.		
		Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.
Vap. press. at 100°	Obs.	1768	787	715	62·7	5·66	9·48
in mm. × 100	Corr.	1950 (2028)	867 (910)	803	94·4	7·81	91·8
Critical solution temp. in water		All very high			All very high		
Increase of Q in benzene		(0·5)	(0·3)	4·5	4·5	5·0	14·3

Compound.		Nitroaniline.			Nitroacetanilide.		
		Ortho-.	Meta-.	Para-.	Ortho-.	Meta-.	Para-.
Vap. press. at 100°	Obs.	65·2	12·9	1·36*	9·05	0·42*	0·21*
in mm. × 100	Corr.	73·2	15·9	3·18	11·7	0·74	0·84
Critical solution temp. in water		211·0°	187·5°	172·5°	198·0°	180·0°	178·0°
Increase of Q in benzene		12·2	15·6	23·4	14·8	86·6	92·1

extent; their solubilities in water (so far as these can be followed) are of the same order, and the rise of the heat of solution in benzene is small, even with the para-compound. The introduction of an acetyl group increases the differences between the isomerides, but not very greatly. This is perceptible in all the three properties concerned.

The nitroanilines are distinctly abnormal, although not much more so than the chloroacetanilides; the differences are in the usual direction, the ortho- having much the highest vapour pressure, and being least soluble in water and most soluble in benzene, whilst the para- comes at the opposite end of the scale, and the meta- stands much nearer to the para-. The introduction of an acetyl group again accentuates the differences, and the nitroacetanilides show marked abnormality. The effect on the vapour pressure is discussed below. The nearness of the critical solution temperatures of meta- and para- is to be noticed: these values for the three compounds reproduce, although on a smaller scale, the relations found among the nitrophenols. It is clear that as regards the properties we are considering, aniline and acetanilide resemble benzoic acid rather than phenol, in that their chlorine derivatives are normal, which the chlorophenols are not. All these compounds form abnormal nitro-derivatives; the abnormality of the nitroanilines and nitroacetanilides is of the same type as that of the hydroxybenzoic acids and the nitrophenols, and does not present the peculiarities which occur among the nitrobenzoic acids.

It will be noticed that among both the chloro- and the nitroacetanilides (but not among the corresponding anilines) the vapour pressure of the meta- is lower than that of the para-compound; the difference with the nitro-compounds is small, and only appears in the corrected values, but in the chloro-derivatives it is large. It is only rarely that this relation is found among aromatic derivatives, and it has been pointed out (Sidgwick, T., 1920, **117**, 395) that it is practically confined to compounds in which one substituent is an amino- or a substituted amino-group. The dimethylchloroanilines apparently exhibit a small difference in this direction (boiling points: meta-, 231—233°, para-, 230—231°), but in other cases the effect is much more marked, as the following examples show [the compounds are indicated by means of the two substituents alone; the figure which follows is the number of degrees difference between the boiling point of the meta- (which is always the higher) and that of the para-compound]: $CH_3O{:}NH_2$, 11°; $NH_2{:}NH{\cdot}CH_3$, 10°; $NH_2{:}NH{\cdot}C_2H_5$, 14°; $NH_2{:}N(CH_3)_2$, 7°; $NH_2{:}N(C_2H_5)_2$, 16°; $N(CH_3)_2{:}N(CH_3)_2$, 8°.

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CX.—*Photocatalysis. Part I. The Synthesis of Formaldehyde and Carbohydrates from Carbon Dioxide and Water.*

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THE photosynthesis of carbohydrates in the living plant unquestionably forms one of the most interesting problems in chemistry, and up to the present it has been very far from being understood. Many experimental results have been published, but no very definite conclusions can be drawn from them. Thus it does not seem definitely to have been established whether or no formaldehyde is actually the first stage in the synthetic process, assuming, of course, that the initial materials are carbon dioxide and water. One of the difficulties met with is the absence of proof that formaldehyde exists in growing leaves as a definite intermediate stage. There is no doubt that the general concensus of opinion is in favour of the view that formaldehyde is photochemically synthesised from carbon dioxide and water, although theories differ as to the chemistry of the process, and that the formaldehyde is then polymerised to form carbohydrates.

On the other hand, Moore and Webster (*Proc. Roy. Soc.*, 1914, [*B*], **87**, 163, 556; 1918, [*B*], **90**, 168) seem to take the view that formaldehyde does not form one of the stages in the phytosynthesis of carbohydrates, because they say that, if formaldehyde were formed, it would combine to form stable complexes with the proteins, and this would prevent its polymerisation to form sugars. This opinion is somewhat striking in the light of the experimental evidence published by these authors. They have undoubtedly proved (1) that formaldehyde is formed by the action of ultra-violet light on carbon dioxide and water in the presence of certain inorganic "catalysts," and (2) that formaldehyde is polymerised to reducing sugars in ultra-violet light. Clearly, therefore, carbohydrates can be synthesised from carbon dioxide and water under certain conditions in two stages. On the other hand, Moore and Webster have found that chlorophyll and all organic substances of biochemical origin give formaldehyde on exposure to ultra-violet light, and thus it would seem that the photosynthesis of biochemical substances from formaldehyde does not take place in the plant. Moore and Webster's results are therefore, in a sense, contradictory, and their evidence does not seem to bring the problem very much nearer solution.

We have made a number of experiments on photosynthesis, and as the result of these are able to state that it is possible to synthesise carbohydrates from carbon dioxide and water in light and that formaldehyde does form the first stage in the photosynthetic process. It is well known that carbon dioxide absorbs ultra-violet light of very short wave-length ($\lambda = 200\mu\mu$), and that formaldehyde absorbs ultra-violet light of longer wave-length ($\lambda = 290\mu\mu$). Hence, the ultra-violet light which will act on an aqueous solution of carbon dioxide has a much shorter wave-length than that which will act on an aqueous solution of formaldehyde, and if the photosynthesis of the carbohydrates from carbon dioxide and water takes place in two stages (formaldehyde formation and subsequent polymerisation), light of two different wave-lengths will be required.

The first point to be proved was whether an aqueous solution of carbon dioxide gives formaldehyde on exposure to light of very short wave-length. Moore and Webster state that no formaldehyde is formed, but this statement is incorrect. It is perfectly true that if water saturated with carbon dioxide is exposed in quartz vessels to sunlight or the light from the quartz mercury lamp, no formaldehyde is to be found in the solution. If, however, during the exposure carbon dioxide is passed through the water, very definite evidence is obtained of the formation of formaldehyde. The explanation of Moore and Webster's failure to discover formaldehyde is to be found in the fact that when the solution of carbon dioxide is not agitated the formaldehyde produced is polymerised to carbohydrates as fast as it is formed. When the solution is agitated, some of the formaldehyde is carried to the back of the quartz vessel, where it is more protected from the light. A small amount therefore escapes polymerisation, and this can very readily be detected by Schryver's test. We have further found that when the carbonic acid solution is exposed in thin glass vessels to the light, no formaldehyde is produced, which clearly proves that the effective light has a very short wave-length.

We have also investigated the effect of ultra-violet light on aqueous solutions of formaldehyde, and find, as did Moore and Webster, that polymerisation to active or reducing sugars readily takes place. Moreover, if the formaldehyde solutions are exposed in thin glass vessels, the polymerisation still takes place, although much more slowly. It is thus evident that the effective light has a greater wave-length than that required for the synthesis of formaldehyde from carbon dioxide and water, so that if a solution of carbonic acid be exposed to ultra-violet light and protected from those specific rays which cause the polymerisation, the amount of formaldehyde formed in the solution will be increased. It is quite possible to find a solution which selectively absorbs these rays while being transparent to the very short wave-length rays. If such a substance does not interfere in any chemical sense, it may be added to the water through which the carbon dioxide is being passed. We find that paraldehyde fulfils these conditions. A solution of paraldehyde in CO_2-free water gives no formaldehyde on exposure to light, and a solution of formaldehyde containing paraldehyde is stable to light, that is to say, the paraldehyde completely protects the formaldehyde from those rays which cause its polymerisation. We then found that an aqueous solution of paraldehyde containing carbon dioxide gives a very good yield of formaldehyde on exposure to the light from the quartz lamp. The paraldehyde does not act as a catalyst in the formation of formaldehyde, but merely as a protector of the formaldehyde when formed. An exactly similar result is obtained with sodium phenoxide. In the absence of carbon dioxide, no formaldehyde is formed, a solution of formaldehyde is not polymerised by light in the presence of sodium phenoxide, but a solution of sodium phenoxide in the presence of carbon dioxide on exposure to ultra-violet light gives a good yield of formaldehyde.

Exactly the same explanation applies to the metallic salts, ferric chloride, uranium nitrate, etc., which Moore and Webster say are "catalysts," for it appears that they do not catalyse the production of formaldehyde, but merely protect it when formed. We have proved this by direct observation of the stability of formaldehyde solutions containing these "catalysts" on exposure to light, and have confirmed it by light absorption experiments which establish the fact that each "catalyst" selectively absorbs those rays which polymerise formaldehyde. We have also found that 1 per cent. solutions of ferric chloride and uranyl nitrate which contain carbon dioxide give good yields of formaldehyde when exposed in quartz tubes to the light, but do not do so when a thin glass screen is interposed. The glass screen removes the very short wave-length rays which cause the formation of the formaldehyde.

It is not surprising that Moore and Webster fell into error in interpreting the function of their inorganic "catalysts," since they failed to observe any formation of formaldehyde in the absence of one of these salts, but it is curious that they did not realise the explanation of this non-production of formaldehyde, since they themselves were the first to prove that, when unprotected, the formaldehyde is polymerised to reducing sugars. It is obvious that Moore and Webster's conclusions as regards the phytosynthetic process are very materially affected. They state that the process depends on the presence of iron salts and go to some trouble to prove the presence of iron in the chloroplast. It is evident, however, that, so far from being a catalyst, the iron is really an anticatalyst, for, in the first place, it does not catalyse the formation of formaldehyde, and, in the second, it prevents the formaldehyde from polymerising to carbohydrates. Indeed, the presence of iron, if in sufficient concentration to act in the way Moore and Webster suggest, will be inimical to the growth of the plant, since the amount of formaldehyde produced will steadily increase until the plant is poisoned.

Two of the catalysts employed by Moore and Webster fall into a different category, namely, colloidal uranium hydroxide and colloidal ferric hydroxide. The explanation of the rôle played by these substances is discussed below.

Reference has been made to Moore and Webster's discovery that all substances of biochemical origin give formaldehyde when exposed in aqueous solution to ultra-violet light. This bare statement of fact is liable to mislead, because it would seem to give support to the view that these substances cannot be built up by the plant from formaldehyde. We have confirmed many of these observations, but we also find that reducing sugars are produced at the same time. Thus, whilst it is perfectly true, for instance, that a 5 per cent. aqueous solution of glycerol gives some formaldehyde on exposure to the quartz mercury lamp, a considerable amount of a reducing sugar is also produced. After only three hours' exposure to the light, sufficient sugar is produced to give a marked reduction of Benedict's solution, the total amount of sugar formed being equivalent in reducing power to 0·04 gram of glucose.

Many other substances besides those of biochemical origin give similar results, and amongst these acetone may be mentioned. An aqueous solution of acetone (1 per cent.), after some hours' exposure, gives some formaldehyde and a considerable quantity of sugar. It is well known that acetone, when photochemically decomposed, does not give formaldehyde as a direct product of decomposition, but yields formic acid, carbon dioxide, methane, etc., according to the amount of free oxygen present in the solution. It is obvious, therefore, that the formaldehyde must have been produced by photosynthesis from the carbon dioxide and water, and the question at once arises as to whether the same explanation does not apply to all carbohydrates and to chlorophyll, namely, that under the influence of light of very short wave-length they are decomposed to carbon dioxide, which is photosynthesised to formaldehyde, and this in its turn is photopolymerised to sugars.

There is no question but that under the influence of ultra-violet light an equilibrium is set up between reducing sugar, carbon dioxide, and formaldehyde, and in all probability the equilibrium may be represented by

$$\begin{tikzcd}
\text{Sugar} \arrow[rr] & & \text{Carbon dioxide} \arrow[dl] \\
& \text{Formaldehyde} \arrow[ul] &
\end{tikzcd}$$

The existence of this equilibrium is strongly supported by experimental evidence. Thus the polymerisation of formaldehyde to give a recognisable amount of sugar becomes increasingly difficult as its concentration is decreased. Again, the polymerisation will be materially enhanced if the concentration of the carbon dioxide be increased by the addition of sodium carbonate, as shown by Moore and Webster, or, better still, as we have found, of potassium bicarbonate.

It must be remembered that this equilibrium is established in ultra-violet light, and there is little doubt that the decomposition of the carbohydrate to give carbon dioxide is produced by light of very short wave-length. It is exceedingly doubtful that this decomposition would take place in the growing leaf, where the chlorophyll is only exposed to sunlight after transmission through the epidermis. We feel that Moore and Webster's statement that all substances of biochemical origin give formaldehyde on exposure to light cannot be accepted as an argument that formaldehyde is not the first stage in the photosynthesis of such substances from carbon dioxide and water.

We have already shown that carbohydrates can be photosynthesised from carbon dioxide and water in two stages, but the problem cannot be considered as solved unless it is possible to synthesise carbohydrates from carbon dioxide and water in one and the same vessel, and this we have succeeded in doing. Some difficulty was encountered at first owing to the fact that in the light of the quartz lamp the equilibrium lies very far over to the side of the carbon dioxide, and unless the concentration of this is large the amount of sugar formed is not sufficient to give a positive test. We first exposed saturated solutions of magnesium and calcium bicarbonates to the light from the quartz lamp for many hours, while carbon dioxide was being passed through them. Although strong reactions for formaldehyde were given, stronger than those obtained when a Moore and Webster "catalyst" is used, insufficient sugar was produced to cause reduction of Benedict's solution. A saturated aqueous solution of oxalic acid was then exposed for forty hours to the light. After neutralisation and evaporation, a decided positive reaction for a reducing sugar was obtained. Under the influence of the light, the oxalic acid is decomposed to carbon dioxide, and this gives, in turn, formaldehyde and a reducing sugar. It is probable that the carbon dioxide at the moment of its formation is more active, with the result that the formaldehyde and sugar are more readily produced than from ordinary carbon dioxide in solution.

Reference may also be made to the formation of a reducing sugar when an aqueous solution of acetone is exposed to the quartz lamp. As already stated, formaldehyde is not one of the photochemical decomposition products of acetone, and therefore the formaldehyde and sugar found must have successively been synthesised from the carbon dioxide yielded by the acetone on decomposition.

If a solution of potassium bicarbonate is exposed to the light, a strong reaction is obtained for formaldehyde in a few hours, but insufficient sugar is formed to give a positive test. On the other hand, if a small amount of formaldehyde is added, sufficient reducing sugar is produced, after further exposure for a few hours, to give strong reduction of Benedict's solution.

These results clearly establish the direct synthesis of carbohydrates from carbon dioxide and water, with formaldehyde as an intermediate stage, and they also establish the fact that no catalyst is necessary. It is further evident that the equilibrium between sugar, formaldehyde, and carbon dioxide existing in the unshielded light of the lamp lies very far over to the side of carbon dioxide.

However satisfactory these results may appear to be, they do not by any means give a complete explanation of the actual process which is taking place in the plant. There is present in ordinary daylight only a very small amount of light of wave-length $\lambda=200\mu\mu$, which is necessary for the first, or formaldehyde, stage. Moreover, it is obvious that the plant juices and pigments completely absorb the ultra-violet rays, so that the phytosynthesis, if dependent on these rays, could not take place. Plants grow, and during their growth synthesise carbohydrates in light transmitted through glass which completely absorbs the ultra-violet beyond $\lambda=350\mu\mu$. Finally, no formaldehyde is formed from carbon dioxide and water under the influence of light transmitted through glass. Clearly, therefore, the vital process differs markedly from the laboratory experiments already described, and the difference is that the plant uses light of longer wave-length than $350\mu\mu$, that is to say, light which is almost entirely comprised within the visible region of the spectrum. We have found that the solution of the problem lies in photocatalysis, and we have succeeded in synthesing active or reducing sugars directly from carbon dioxide and water in two stages with the aid of suitable photocatalysts in light of longer wave-length than $350\mu\mu$, such as is used by the living plant.

In recent papers, it has been shown by one of us (Baly, *Phil. Mag.*, 1920, [vi], **40**, 1, 15) that the frequencies characteristic of any molecule in the ultra-violet are exact integral multiples of a fundamental, infra-red frequency also characteristic of that molecule, and, further, this infra-red frequency is an exact integral multiple of the frequencies characteristic of the atoms composing that molecule. Again, a definite amount of energy is required to cause a molecule to undergo a specific reaction, and this energy may be supplied to that molecule either in the form of one quantum at the ultra-violet frequency or as a whole number of quanta at one of the infra-red frequencies characteristic of the molecule or its component atoms. When the energy is absorbed at the ultra-violet frequency, the reaction is known as photochemical, and the synthesis of formaldehyde and its subsequent polymerisation by ultra-violet light are pure photochemical reactions.

It has recently been shown (Baly and Barker, this vol., p. 653) that in the photochemical reaction between hydrogen and chlorine the energy radiated during the reaction by the hydrochloric acid is partly reabsorbed by the surrounding chlorine, with the result that a great deal more chlorine and hydrogen react than corresponds with the amount of light absorbed. In this case the chlorine is activated partly by absorbing light of its own characteristic ultra-violet frequency and partly by absorbing the infra-red light radiated by the hydrochloric acid that is being formed.

It should be possible, therefore, to cause the substance A to undergo a photochemical reaction in light of a frequency which is not absorbed by the substance A. If a substance B, having exactly the same infra-red frequencies as A, be mixed with A, and the two be exposed to light which is absorbed by B and not by A, then the energy radiated by B in the infra-red will be absorbed by A, with the result that A will undergo the photochemical reaction. B then acts as a true photocatalyst. The criteria defining a photocatalyst are, first, that it has exactly the same infra-red frequencies as the catalyte, and, secondly, that it has a different frequency in the visible and the ultra-violet regions from the catalyte.

A typical example of photocatalysis was described by Daniels and Johnson (*J. Amer. Chem. Soc.*, 1921, **43**, 72), who showed that nitrogen pentoxide is not decomposed by blue light except in the presence of nitrogen peroxide, which absorbs blue light. The energy thus absorbed by the nitrogen peroxide is radiated at frequencies in the infra-red which are exactly the same as those of the nitrogen pentoxide, the two compounds having the same atoms.

There is no doubt that the phytosynthesis of carbohydrates in the living plant from carbon dioxide and water is a photocatalytic one, and in all probability chlorophyll or carotin is the photocatalyst. The photocatalysis consists in the absorption of light of longer wave-length than 350 $\mu\mu$ by the chlorophyll or carotin and the radiation of this energy at infra-red frequencies which are reabsorbed, with the result that the carbon dioxide forms successively formaldehyde and carbohydrates. If this is the correct explanation, then it should be possible to carry out the synthesis in the laboratory, using visible light and a photocatalyst.

Since the two stages require for their experimental realisation light of different wave-lengths, they may be discussed separately. A suitable photocatalyst for the synthesis of formaldehyde from carbon dioxide and water is found in a coloured basic compound such as malachite-green, or *p*-nitrosodimethylaniline. An aqueous solution of either of these compounds saturated with carbon dioxide gives formaldehyde on exposure to light behind a thick plate-glass screen. In the absence of carbon dioxide, no formaldehyde is produced with either of the photocatalysts. A similar result is obtained with methyl-orange and with other substances.

It would seem that in the case of colloidal uranium and ferric hydroxides Moore and Webster did use true photocatalysts. There is little doubt that in each case some combination with the carbon dioxide takes place, so that the conditions for the photocatalysis are secured. This will explain why in the presence of these two substances formaldehyde is produced from carbon dioxide in visible light, as shown by Moore and Webster. It cannot be claimed that any of the photocatalysts mentioned are perfect, since they do not necessarily protect the formaldehyde entirely from the rays which polymerise it. Moore and Webster established this fact by obtaining an increased yield of formaldehyde with the colloidal uranium hydroxide solution when the vessel was surrounded by a solution of chlorophyll in alcohol. It must again be pointed out that, although the colloidal hydroxides of uranium and iron apparently act as photocatalysts in the formation of formaldehyde, they also largely protect the formaldehyde, when formed, by virtue of their power of absorbing the long-wave, ultra-violet rays. They thus prevent its polymerisation to carbohydrates, and therefore neither of them would be of any use to the growing plant.

Our results show conclusively, not only that it is possible to produce formaldehyde from carbon dioxide and water by the direct action of light of very short wave-length ($\lambda = 200\ \mu\mu$), but that it is also possible to produce the formaldehyde from carbon dioxide and water in visible light in the presence of a photocatalyst. They also entirely dispose of Moore and Webster's contention that the photocatalyst must be inorganic, since, although the metallic salts used by them are not catalysts at all, but protectors, the colloidal uranium and ferric hydroxides appear to act as photocatalysts, and for this purpose coloured organic bases act equally well.

For the second stage of the synthesis, namely, the polymerisation of formaldehyde to give active or reducing sugars, it will be necessary to employ as photocatalyst a coloured substance which forms a complex with the formaldehyde in order to secure the exact similarity between the infra-red frequencies. A suitable substance is not readily obtained, but the following experiment leaves no doubt of the photocatalysis of this polymerisation. An aqueous solution containing 17 per cent. of sodium citrate and 9 per cent. of sodium carbonate, on exposure to the quartz mercury lamp for two hours, gives formaldehyde and sufficient sugar to cause marked reduction on the addition of 1 per cent. of copper sulphate and warming. This formation of sugar does not occur if the alkaline solution is exposed to the same light behind a screen of thick plate-glass. On the other hand, Benedict's solution, which contains the same proportions of the three compounds, gives marked reduction after exposure to the light for two hours behind the plate-glass screen. This definitely establishes the photocatalysis, for the formation of the formaldehyde and its polymerisation to sugar take place within the citrate complex, which, since it contains copper, has the power of absorbing visible light, and the energy so absorbed is sufficient to cause the polymerisation to take place.

Whilst two stages in the synthesis of a reducing sugar have thus been photochemically carried out in the laboratory with and without a photocatalyst, the plant is able to synthesise carbohydrates from carbon dioxide without the formation of formaldehyde in sufficient quantities for its ready recognition in the growing leaf. It must be remembered that, if a suitable substance were obtained capable of photocatalysing both reactions in the laboratory, the separate existence of formaldehyde would not be capable of proof, since the carbon dioxide and water would give formaldehyde and carbohydrate within the same complex. We have not as yet been able to find a photocatalyst capable of acting in the dual capacity on a solution of carbonic acid, but it would seem that chlorophyll is an ideal substance for the dual rôle. Whereas every photocatalyst that we have used for the first stage does not form complexes with the formaldehyde that is produced, chlorophyll, by virtue of its structure, would seem to be capable of associating itself with carbon dioxide and retaining the formaldehyde when formed, with the result that the process passes through the two stages to give the carbohydrate. We lay great stress on this point. The evidence in favour of the existence of free formaldehyde in growing leaves is not at all strong and thus definite proof that formaldehyde is the intermediate stage in carbohydrate synthesis is wanting. The results now brought forward certainly support the view that formaldehyde is an intermediate stage, and they also go to prove that its free existence in the leaf is not to be expected. Failure to establish its presence by the most delicate of tests can no longer be accepted as evidence against its being the first stage in the phytochemical synthesis of carbohydrates. We have not as yet carried out any experiments with chlorophyll, because we wished in the first instance to deal with the problem in the simplest possible way and to make use of photocatalysts the action of which is as simple and straightforward as possible. The use of chlorophyll at once introduces the possibility of the synthesis of optically active sugars, and we hope to investigate the behaviour of chlorophyll in the immediate future.

It is evident that the equilibrium between carbohydrate, formaldehyde, and carbon dioxide existing in the unshielded light of the mercury lamp will be entirely disturbed by a photocatalyst. In the presence of a photocatalyst which carries the reaction right through from carbon dioxide and water in visible light, the equilibrium will be shifted entirely to the carbohydrate side, since the system will be screened from those rays which decompose the carbohydrate. For this reason, as is the case in the living plant, carbohydrates will be formed when the concentration of the carbon dioxide is very small.

Conclusions.

1. An aqueous solution of carbon dioxide gives formaldehyde when exposed to light of very short wave-length ($\lambda = 200\ \mu\mu$).
2. An aqueous solution of formaldehyde is polymerised to reducing sugars in light of wave-length 290 $\mu\mu$.
3. In the presence of paraldehyde, sodium phenoxide, and certain metallic salts which absorb light of wave-length 290 $\mu\mu$, the yield of formaldehyde is materially increased. These substances do not catalyse the reaction, but protect the formaldehyde, when formed, from polymerisation.
4. The photosynthesis of formaldehyde from carbon dioxide and water can be photocatalysed by certain coloured basic substances, for example, colloidal uranium and ferric hydroxides, malachite-green, methyl-orange, etc. The photosynthesis then takes place in visible light.

5. The polymerisation of formaldehyde to give carbohydrates has also been photocatalysed.

6. When carbohydrates, glycerol, acetone, oxalic acid, etc., are exposed in aqueous solution to the light from the quartz mercury lamp, formaldehyde and reducing sugars are formed. An equilibrium is set up between sugar, formaldehyde, and carbon dioxide.

7. When exposed to the unscreened light from the mercury lamp, this equilibrium apparently lies far over to the side of the carbon dioxide.

8. By the action of the light from the mercury lamp on a concentrated solution of potassium bicarbonate considerable quantities of formaldehyde are produced, but insufficient to give a positive test for a sugar. If, however, more pure formaldehyde is added, a positive test for a reducing sugar will be obtained after further exposure for a few hours.

9. In the presence of a photocatalyst capable of catalysing both stages of the reaction, the equilibrium will be shifted entirely over to the side of the reducing sugar.

10. Chlorophyll would seem to be an ideal photocatalyst for both stages of carbohydrate synthesis from carbon dioxide and water. The formation of carbohydrates in the growing leaf from very small concentrations of carbon dioxide without the free existence of formaldehyde as an intermediate product is thus explained.

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CXI.—*α-Monosodium Glyceroxide : Its Structure and Application.*

By ARTHUR FAIRBOURNE and HAROLD TOMS.

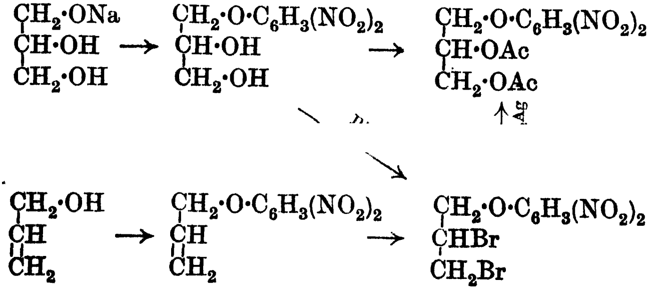
UP to the present the general methods of attempted identification of the structure of monoglycerides have depended either on the action of glyceryl chlorohydrins on the salts of fatty acids or on the esterification of the fatty acids with the chlorohydrins and the subsequent exchange of the halogen atoms for hydroxyl groups (*Annual Reports*, 1920, **17**, 58). Fischer has shown these methods to be untrustworthy (*Ber.*, 1920, **53**, [*B*], 1621), and there has now been published an alternative and trustworthy method based on the constitution of "acetone glycerol" (Fischer, Bergmann, and Barwind, *Ber.*, 1920, **53**, [*B*], 1589).

The present authors found it necessary to determine the exact constitution of certain monoglycerides in the course of a larger investigation on the preparation of oxazines, but in view of the current interest in this problem it is felt desirable that these experiments should now be communicated separately, since they embody an independent and quite different method of preparation of α-monoderivatives of glycerol of undoubted purity.

Willgerodt (*Ber.*, 1879, **12**, 766) condensed glycerol, in the presence of potassium hydroxide, with 1-chloro-2 : 4-dinitrobenzene, then called "α-dinitrochlorobenzol," whence he named the product "monoalphadinitrophenylglycerinäther," the letter of identification, however, being used apparently without reference to the position of substitution in the glyceryl radicle, a terminology which would seem to be largely responsible for this ether subsequently remaining in the literature, without proof, as definitely an α-ether of glycerol.

Löbish and Loos (*Monatsh.*, 1881, **2**, 782, 842) prepared both the mono- and di-sodium derivatives of glycerol, no attempt being made to prove the constitution of either compound. Letts (*Ber.*, 1872, **5**, 159) also prepared the mono-sodium derivative, removing the accompanying molecule of alcohol of crystallisation by heating the crystalline product in a current of hydrogen, and Nef (*Annalen*, 1904, **335**, 285), whilst working on the dissociation of this substance, obtained indirect evidence that it was probably the α-compound.

In the present work, this derivative has been prepared in large quantity, quite free from alcohol, by warming the precipitated powder in an evacuated flask. The product was then condensed with 1-chloro-2 : 4-dinitrobenzene to give an ether of necessarily the same constitution as that of the sodium derivative, and this constitution has been successfully determined by proof of the identity of its diacetyl derivative with that obtained from the 2 : 4-dinitrophenyl ether of allyl alcohol, and confirmed by the identity of the dibromides obtained from the glyceryl and the allyl ethers respectively.



EXPERIMENTAL.

α-Monosodium Glyceroxide, $CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot ONa$.

Twenty-three grams of sodium (1 mol.) were dissolved in 350 c.c. of absolute alcohol, and to this was cautiously added slightly less than one molecular proportion of glycerol. The addition of each portion caused a violent action and the precipitation of a white, crystalline solid, which was filtered rapidly and washed with alcohol and then with ether. The yield, calculated as $C_3H_7O_3Na,C_2H_5\cdot OH$, was nearly theoretical (Found: Na=14·22; $C_2H_5\cdot OH$=28·5. $C_3H_7O_3Na,C_2H_5\cdot OH$ requires Na=14·37; $C_2H_5\cdot OH$=28·7 per cent.).

The alcohol of crystallisation was removed from this compound by heating it for five hours at 100° and 25 mm. pressure, a modification of this method being used in the estimation of the alcohol in the original compound. The percentage of sodium was estimated in the alcohol-free glyceroxide obtained in this way (Found: Na=19·94. $C_3H_7O_3Na$ requires Na=20·17 per cent.).

Glycerol α-2 : 4-Dinitrophenyl Ether, $C_6H_3(NO_2)_2\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$.

Molecular proportions of α-monosodium glyceroxide (11·4 grams) and 1-chloro-2 : 4-dinitrobenzene (20·25 grams) were dissolved in 104 c.c. and 206 c.c. of glycerol respectively. When these solutions had cooled to about 100°, the chlorodinitrobenzene solution was poured into that of the glyceroxide, which immediately assumed a cherry-red colour. The mixture was heated almost to boiling for twenty minutes, and was then poured into 1180 c.c. of water, the precipitated material being redissolved by boiling. After keeping for twenty-four hours, the mass of yellow crystals was filtered off and washed with light petroleum (b. p. 40—60°), the yield being 90 per cent. of the theoretical.

This ether is, when pure, colourless, and it crystallises from water, benzene, and tetrachloroethane. It is soluble in ether, alcohol, and acetone, and in alkaline solution is deep red; but it becomes colourless on the addition of a slight excess of acid. It melts at 85° (compare Willgerodt for an ether of unknown constitution, m. p. 83°; *Ber.*, 1879, **12**, 769).

The Diacetyl Derivative,
$C_6H_3(NO_2)_2\cdot O\cdot CH_2\cdot CH(O\cdot CO\cdot CH_3)\cdot CH_2\cdot O\cdot CO\cdot CH_3$.
—The glycerol ether was heated under reflux for two to three hours with five parts of acetic anhydride and one part of anhydrous sodium acetate. The oil, obtained by pouring the mixture into

water, dissolved on boiling, and on cooling reappeared as a colourless, crystalline substance. It crystallises from water and from alcohol, and melts at 106—107° (Found: $CH_3\cdot CO=25\cdot12$, $25\cdot13$. $C_{13}H_{14}O_9N_2$ requires $CH_3\cdot CO=25\cdot15$ per cent.).

2 : 4-*Dinitrophenyl Allyl Ether.*

This compound was prepared by a method similar to that used by Willgerodt (*loc. cit.*), who distilled off the excess of allyl alcohol after condensation had taken place. It has been found that this procedure leads in most cases to charring, and in one instance an explosion occurred. Instead, therefore, of distilling off all the allyl alcohol, some 80 per cent. only was removed in this way, the residue being poured into a 5 per cent. solution of sodium chloride and extracted with ether. The fibrous mass obtained after the removal of the ether crystallised from alcohol in long, colourless needles, m. p. 46°.

Several unsuccessful attempts were made to oxidise this substance directly to the corresponding dihydroxy-compound, and this method of identifying the structure of these substances was ultimately abandoned, attention being directed towards the diacetyl and dibromo-derivatives.

2 : 4-*Dinitrophenyl* βγ-*Dibromopropyl Ether*,

$C_6H_3(NO_2)_2\cdot O\cdot CH_2\cdot CHBr\cdot CH_2Br$.

Three grams of 2 : 4-dinitrophenyl allyl ether were dissolved in 10 c.c. of chloroform, and a solution of rather more than the theoretical amount of bromine (2·26 grams) in 10 c.c. of the same solvent was added. The chloroform was distilled off and the residue heated on a water-bath until the excess of bromine had volatilised. The solid thus obtained crystallised in small, hard plates with a silvery lustre, m. p. 110°. The yield was quantitative (Found: $Br=41\cdot76$. $C_9H_8O_5N_2Br_2$ requires $Br=41\cdot67$ per cent.).

Action of Silver Acetate on 2 : 4-*Dinitrophenyl* βγ-*Dibromopropyl Ether.*

Many attempts were made, in various solvents, to replace the bromine in this compound by acetyl radicles, but only in glacial acetic acid solution were any signs of success apparent. The silver acetate used was freshly prepared and analysed in order to check its purity.

Five grams (1 mol.) of pure silver acetate were suspended in glacial acetic acid, and to it was added a solution of 3·6 grams (1 mol.) of the dibromide in the same solvent. The mixture was heated under reflux for four hours, and the silver bromide was then filtered off and washed several times with water. The washings and the filtrate were combined, diluted with water, neutralised with sodium carbonate, and extracted with ether. The solid extracted in this way was a mixture of the required diacetyl compound and unchanged dibromide. By extraction with water and repeated crystallisation from alcohol, a substance was obtained which melted at 104—105°. Further crystallisation had no effect on the melting point, but a mixture with the diacetyl derivative of glycerol α-2 : 4-dinitrophenyl ether melted at 105—106°.

M. p. of the diacetyl derivative of the glycerol ether ...	106—107°
M. p. of the diacetyl derivative of the allyl ether	104—105°
M. p. of the mixed substances	105—106°

The diacetyl derivative obtained indirectly from the allyl ether, therefore, was not perfectly pure, but it was obviously identical with that produced by acetylating the glycerol ether. Since, in the allyl ether, the 2 : 4-dinitrophenyl radicle must be joined to a terminal carbon atom, it follows that the glycerol ether and the sodium derivative are both α-compounds. This conclusion has been definitely confirmed by the identity of the corresponding dibromides in the following manner.

Action of Phosphorus Tribromide on Glycerol α-2 : 4-*Dinitrophenyl Ether.*

This substance was warmed gently for an hour with phosphorus tribromide, and when no further evolution of gas occurred the mixture was poured into water. The solid substance obtained after keeping for several days was washed, first with sodium carbonate solution and then with water. After crystallisation from alcohol, the following series of melting points was obtained :

M. p. of this product	110°
M. p. of the dibromide of the allyl ether	110°
M. p. of the mixed substances	110°

The identity of these melting points affords an independent proof of the structure of the monosodium glyceroxide and of the dinitrophenyl ether derived from it.

The constitution of the α-monosodium derivative being now proved, it is thus possible to prepare mono-substituted products of glycerol by treating this sodium compound with acid chlorides or compounds of a similar nature, as has been done in the case of the dinitrophenyl ether described above. A typical example of mono-acyl preparations (glycerides) is that of the benzoyl ester, the constitution of which as an α-derivative has been proved by the following representative experiment.

Equimolecular proportions of α-monosodium glyceroxide and benzoyl chloride were placed in dry benzene and kept for twenty-four hours. The mixture was then heated for a few minutes and filtered. The benzoyl glyceride was obtained as a viscous oil, which crystallised after being subjected to a freezing mixture of ice and salt for two days (Found: $C_6H_5{\cdot}CO=53{\cdot}60$. $C_{10}H_{14}O_4$ requires $C_6H_5{\cdot}CO=53{\cdot}56$ per cent.).

The authors wish to take this opportunity of expressing their thanks to Professor Smiles for the interest he has taken in this work.

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CXII.—*Electrochemical Conceptions of Valency.*

By JOHN ALBERT NEWTON FRIEND.

THEORIES of valency may be divided into two groups, namely, physical and chemical. Physical theories are intimately concerned with the constitution of the atom, and the nature of the forces causing chemical combination. Chemical theories, on the other hand, postulate the existence of either definite or indefinite attractive forces, and deal more particularly with the structure of the molecule entering into chemical reactions. Chemical theories, therefore, do not necessarily stand or fall with the physical theories, and the valency bond assumed to join sodium and chlorine atoms in sodium chloride may still be written Na–Cl, irrespective of whether the physicist regards it as a mechanical hook, a tube of force, or as marking the passage of an electron.

Sir J. J. Thomson has recently published (*Phil. Mag.*, 1921, [vi], **41**, 510) a more complete account of his physical theory of valency, which was described in 1914 (*Phil. Mag.*, 1914, [vi], **27**, 757) and has been adapted to harmonise with modern conceptions of atomic structure. His theory offers such interesting physical interpretations and support for many of the essential features of the purely chemical theory of valency suggested by the present author in 1908 (T., 1908, **93**, 260) that it seems desirable to direct attention to the more important points.

Thomson distinguishes two kinds of valency.

(i) *Ionised Valency*.—When a highly electropositive atom, such as sodium, comes into contact with a strongly electronegative atom, like chlorine, the latter is sufficiently powerful to drag an electron from the former, with the result that the sodium becomes positively charged and the chlorine negatively. Compounds of this character have abnormal specific inductive capacities, ϵ, and do not conform to Maxwell's law that

$$\epsilon = n^2$$

where n=refractive index.

Thomson terms this electronic interchange *intramolecular ionisation*, and the bond of union thus created corresponds with the *polar* valence of Bray and Branch (*J. Chem. Amer. Soc.*, 1913, **35**, 1440), the *mobile* valence of Lewis (*ibid.*, p. 1448), and the *free* valencies of the author's theory (T., 1908, **93**, 260), according to which the sodium exerts a free positive valence, and the chlorine a free negative valence. This may be represented as $\mathrm{Na} \longrightarrow \mathrm{Cl}$, the positive atom being termed the *donor* and the negative the *acceptor*.

(ii) *Non-ionised Valency*.—When two electrochemically similar atoms unite, as, for example, in the case of the elementary gases hydrogen, oxygen, etc., Maxwell's law applies and Thomson assumes that no electron actually passes from one atom to the other, so that neither atom may be said to be charged. The forces joining the atoms thus correspond with the *non-polar* valencies of Bray and Branch, and the *immobile* valencies of Lewis.

There is this important feature, however, that the valency electron of each atom starts a tube of force which anchors itself upon the nucleus of the opposite atom. This may be represented * as $\mathrm{H} \rightleftharpoons \mathrm{H}$, in the case of hydrogen, so that these non-ionised or immobile valencies *are always exerted in pairs of equal and opposite sign*, and thus correspond with two valency bonds.

This is a very striking physical interpretation of the author's residual or latent valencies " which differ from the above-mentioned free valencies in that *they can only be called out in pairs of equal and opposite sign* " (T., 1908, **93**, 263). The italics occur in the original. These residual valencies were postulated in order to account for polyatomic or diatomic molecules composed of atoms of similar electrochemical behaviour, because it was regarded as unlikely that in a molecule of oxygen, for example, one atom could be differently charged from the other, as the ordinary electrochemical theory of valency would require, and as was postulated in the Brodie-Schönbein theory of ozone and antozone. At the time there were several difficulties in the way of accepting the author's theory. One lay in understanding how a pair of equal and opposite forces could be called into play. Thomson's explanation disposes of this. A second difficulty lay in the fact that hydrogen was rendered bivalent, and this made theoretically possible the existence of polyatomic hydrogen molecules. Thus

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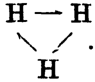
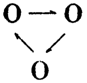
* The half arrow $\rightharpoonup$ may be conveniently used to denote a non-ionised or latent valence, and a full arrow $\longrightarrow$ the passage of an electron, a free or ionised valence.



. Since then, however, the synthesis of triatomic hydrogen, H_3, appears to have been effected (Wendt, *J. Amer. Chem. Soc.*, 1920, **42**, 930), so that the older view of the strictly univalent nature of hydrogen requires revision. The constitution of ozone is presumably similar, the atoms being connected by their latent, immobile, or non-ionised valencies, in cyclic form; thus,



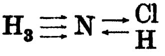
If this formula is correct, the gas should conform to Maxwell's law. As yet, however, the necessary data have not been obtained to confirm this.

Theoretically, polyatomic molecules of all elements are possible, and may be capable of momentary existence, as Thomson and Aston have shown for such substances as CH, CH_2, etc. The deciding factor, however, as to which shall survive must be the degree of stability under normal conditions. It is remarkable that atoms should so frequently arrange themselves in groups of three and multiples of three.

Attention has recently been directed to the fact that ammonium chloride exists in two forms, the transition point being 184·5° (Scheffer, *Verslag. Akad. Wetensch. Amsterdam*, 1915, **18**, 446, 1498) both when moist and dry (Smith, Eastlack, and Scatchard, *J. Amer. Chem. Soc.*, 1919, **41**, 1961). In 1908 the author (*loc. cit.*, p. 267) suggested the existence of two forms, the compound

$$H_3\vdots N \rightleftharpoons Cl\cdot H$$

being first produced, and undergoing intramolecular rearrangement, and ionisation on cooling, to



$$H_3 \overset{\rightarrow}{\underset{\rightarrow}{\rightarrow}} N \overset{\rightarrow}{\leftarrow} \begin{matrix}Cl\\H\end{matrix}$$

Evidence in favour of the former formula as representing the initial product is not only found in the ease with which the salt dissociates on heating to ammonia and hydrogen chloride, but also in the fact that ammonia and hydrogen chloride, even when perfectly dry, unite in benzene solution (Kahlenberg, *J. Physical Chem.*, 1902, **6**, 1). The reaction is thus molecular, not ionic. These observations are in harmony with the views of Thomson, who regards the forces generating molecular compounds as similar to non-ionised valencies, and shows that the union of one molecule with another molecule, radicle, or atom may lead to greater stabilisation and even to intramolecular ionisation amongst atoms not exhibiting it originally.

There would appear to be no essential chemical difference between ionised and non-ionised valencies by which they can be distinguished. Thomson's test, which consists in the application of Maxwell's law, can only be utilised in a few cases. A study of his short list of substances conforming to Maxwell's law reveals the interesting fact that these do not exhibit electrolytic dissociation in aqueous solution, for example, hydrogen, carbon monoxide, nitrous oxide. Only in extreme cases, however, can this fact be utilised for the purpose of distinguishing between ionised and non-ionised valencies, since atoms joined by the former are not invariably dissociated in solution.* Thus ammonia does not conform to Maxwell's law, and Thomson therefore places it amongst the molecules manifesting intramolecular ionisation. In aqueous solution, however, the hydrogen atoms do not dissociate from the nitrogen; indeed, such ions as exist in solution containing nitrogen possess a fourth atom of hydrogen, thus, NH_4. As a general rule, electrolytic dissociation occurs only when the ionised valencies connect atoms of high electrical polarity, as in $H \longrightarrow Cl$. There would thus appear to be valencies of all grades of strength, the extremes of which are encountered in non-ionised molecules such as H_2 on the one hand, and intramolecularly ionised molecules such as HCl on the other.

This leads us to the interesting conclusion that there may be two methods of preparing a substance from the same constituents, namely, molecular and ionic. Thus, ammonium chloride may be obtained

1. Ionically—by the union of ammonium and chlorine ions in aqueous solution.
2. Molecularly—by the union of ammonia and hydrogen chloride molecules through non-ionised valencies and subsequent intra-

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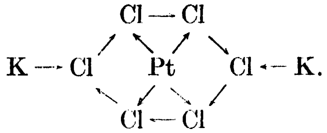
* Contrast Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762.

molecular rearrangement of the $H_3N{:}ClH$, initially produced, to NH_4Cl.

Modern physics, in showing that valency is an electrochemical force, suggests the necessity of remodelling Werner's theory, which postulates an attractive force only, akin to cohesion, and closely resembles the early theory of radicles. The success of the theory has lain in its application to the constitution of complex ions composed of atoms characterised by non-ionised valencies, either in addition to, or independently of, ionised valencies. The theory breaks down entirely when applied to simple inorganic compounds, such as ammonium chloride, containing only ionised valencies. In 1908 the author (T., 1908, **93**, 1007) suggested that in complex salts, the non-dissociated group forms a shell round the heavy metal, the individual atoms being joined by latent or non-ionised valencies. Thus, potassium platinichloride is written as



The chlorine atoms are assumed to lie at the corners of an octahedron enclosing the platinum atom. This is the most stable arrangement. A difficulty lay in understanding how such a shell could be stable. Application of Thomson's theory, however, makes this clear.

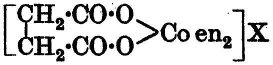
1. The chlorine atoms are joined by non-ionised valencies, so do not dissociate in solution.

2. The field of force due to the charged platinum atom enhances the stability of the non-ionised chlorine valencies in the manner already indicated (see p. 1043), and hence the stability of the shell, although not to such an extent as to cause an actual electronic interchange amongst the chlorine atoms themselves.

The chlorine atoms also tend to attract the platinum atom by stray lines of force, not sufficiently concentrated to produce a definite valency effect, but strong enough to produce effects resembling cohesive forces—to which Thomson ascribes the same origin—which assist in keeping the platinum atom within the shell. The potassium atoms, however, are joined by free or ionised valencies to the chlorine atoms and are hence as free to dissociate in solution as if potassium chloride alone were present.

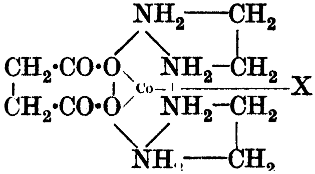
Werner's method of representing the salt, namely, $[PtCl_6]K_2$, may still be adopted, as it is non-committal, save that it shows that the complex within the bracket behaves as one ion.

The shell formula may be applied with equal clearness to the more complex cobaltammines. Thus the succinatodiethylenediaminecobaltic salts



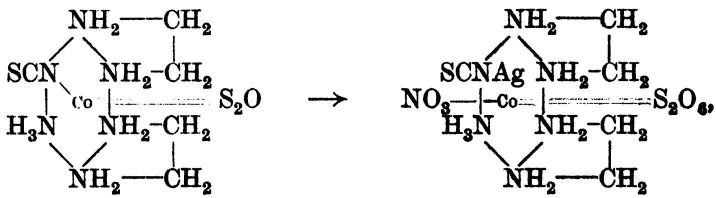
$$\left[\begin{array}{l}CH_2\cdot CO\cdot O\\ CH_2\cdot CO\cdot O\end{array}\!>Co\,en_2\right]X$$

recently prepared by Duff (T., 1921, **119**, 385), contain four nitrogen and two oxygen atoms in the shell; thus,



According to this scheme, several isomerides are clearly possible, namely, with the oxygen atoms in the ortho- (as above) and para-positions, and also with the nitrogen atoms of the different ethylenediamine molecules alternating or interlocked. It is interesting to note that Duff obtained evidence of isomerism in the case of the bromide. The salt obtained by the action of succinic anhydride upon the carbonato-salt was crystalline and presumably had the ortho-form. The salt obtained with free succinic acid was amorphous. Since succinic acid reacts as if it has a configuration analogous to that of fumaric acid (Bruni, *Atti R. Accad. Lincei*, 1904, [v], **13**, i, 626), it is easy to see that the two oxygen atoms would tend to take para-positions in the shell, thus symmetrically separating the two diamine molecules.

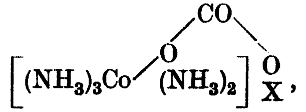
When silver nitrate is added to a solution of *cis-iso*thiocyanatoamminediethylenediaminecobaltic dithionate, $\left[\begin{smallmatrix}SCN\\H_3N\end{smallmatrix}Co\,en_2\right]S_2O_6$, the compound $\left[\begin{smallmatrix}AgSCN\\H_3N\end{smallmatrix}Co\,en_2\right]\begin{smallmatrix}NO_3\\S_2O_6\end{smallmatrix}$ is obtained (Price and Brazier, T., 1915, **107**, 1713). This change in valency of the complex is readily explained by the shell theory. Thus,



the silver attaching itself to the nitrogen in the ring, thus losing its power of separate ionisation. The cobalt has now an extra valence to spare for the NO_3 group, which is ionisable like the

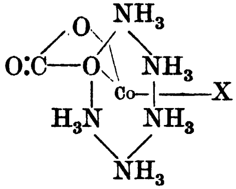
S_2O_6 group, since it is attached to the cobalt atom by a free or ionised valence.

The shell theory explains the constitution of many complex substances which are not capable of direct explanation by Werner's theory. Thus the carbonato-pentamminecobalt salts (Werner and Goslings, *Ber.*, 1903, **36**, 2378; Vortmann and Blasberg, *Ber.*, 1889, **22**, 2648) give no reactions for carbonate ions. Werner suggests the formula



which is clearly a violation of his own theory. The corresponding chromato-derivatives (Briggs, T., 1919, **115**, 67) present precisely the same difficulty, for the CrO_4 radicle is shown to be situated within the complex. In both types, therefore, only one anion is obtained, whereas there should be two.

The shell theory explains this clearly. Thus, the carbonato-derivative is



The cobalt valency is still 3, and the CO_3 group cannot ionise, as it is part of the shell, so that the complex acts as a univalent positive ion.

It will thus be evident that the author's shell theory closely resembles spatially the scheme suggested by Werner, in that the groups are arranged at the corners of an octahedron. It differs from Werner's theory, however, in that:

1. It postulates the existence of such valencies only as are in harmony with modern physical conceptions of the atoms, and is essentially electrochemical.

2. The groups round the central metallic atom are assumed to be joined together by latent or non-ionised valencies and not necessarily to the central atom itself. An explanation is thus afforded for the non-ionising character of the groups in the shell, and the central atom is not endowed with a high number of valencies. Werner's theory does not explain the non-ionising character of the complex ion, since he himself showed that there was no distinction between his "Haupt" and "Neben" valencies.

3. The shell theory explains many phenomena both with simple

inorganic substances * and with complex salts, which cannot be explained by Werner's theory.

4. When models of optically active cobalt complexes are constructed in accordance with the shell theory, it can be shown that the activity is due, not to an asymmetric arrangement round the cobalt atom, as Werner suggested (*Ber.*, 1911, **44**, 1887, etc.), but to the presence of an asymmetric nitrogen atom. The author hopes shortly to deal more fully with this very important point.

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CXIII.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part III. The Partial Reduction of the Dinitrotoluenes by Stannous Chloride and Hydrochloric Acid.*

By Harold Burton and James Kenner.

The partial reduction of aromatic polynitro-compounds is usually carried out by means of either ammonium sulphide or stannous chloride and hydrochloric acid. Further, a nitro-group in the ortho- or para-position to another nitro-group can usually be replaced by an amino-group by heating the compound with alcoholic ammonia. This, however, is, of course, not a reduction process, although instances of it are sometimes quoted as such. It may be said, in fact, that at present our ideas on the relationships of these processes to each other, and on their respective applicabilities, are distinctly vague. Thus Bucherer ("Lehrbuch der Farbstoffchemie," 2nd edition, Leipzig, 1921, p. 197) states that "ersichtliche Gesetzmässigkeiten" may be deduced from a number of instances, which he quotes, of the replacement of a nitro- by an amino-group in polynitro-compounds. This writer evidently has no suspicion that the results obtained are in any way dependent on the reagent employed, and so gives no information on this point. Since, however, reference to the literature shows that illustrations of each of the above three processes are included, and it will now be shown that the result obtained often varies with the reagent, it is evident that Bucherer's collation of results, as it stands, cannot form the basis of any sound conclusions of the kind anticipated.

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* See Rhodes, *Chem. News*, 1921, **122**, 85, 97, who has applied the author's shell theory to hydrates.

Anschütz, who first used stannous chloride for the purpose now under discussion (*Ber.*, 1886, **19**, 2161), obtained 4-nitro-*o*-toluidine from 2 : 4-dinitrotoluene by this means, and at the same time directed attention to the fact that 2-nitro-*p*-toluidine results from the use of ammonium sulphide. But a difference of this kind is not always observed. Thus, the reduction of picric acid first takes place in the 2-position, whatever reagent be employed (Girard, *Annalen*, 1853, **88**, 281; *Jahresbericht*, 1885, 535), whilst from 2 : 4-dinitroaniline both 2-nitro-*p*-phenylenediamine and 4-nitro-*o*-phenylenediamine are obtained by the action of ammonium sulphide (Kehrmann, *Ber.*, 1895, **28**, 1707). In these and in most compounds which have been subjected to partial reduction, the nitro-groups are in the meta-position, and relatively little attention seems to have been given to compounds in which the nitro-groups are in the ortho- or para-position to each other. Nevertheless, it has long been known that the application of the ammonium sulphide process to compounds containing a mobile substituent in these positions relative to a nitro-group results, not in the reduction of the nitro-group, but in the replacement of such mobile substituent by a group containing sulphur (Beilstein and Kurbatow, *Ber.*, 1878, **11**, 2056). It is true that 2-nitro-*m*-toluidine is stated to have been prepared in this way from 2 : 3-dinitrotoluene (Limpricht, *Ber.*, 1885, **18**, 1402; Noelting and Stoecklin, *ibid.*, 1891, **24**, 565), but it will be shown that the genuine 2-nitro-*m*-toluidine has quite other properties than those ascribed to his product by Limpricht. It has already been demonstrated that the chief product of the action of ammonium sulphide in this case also is dinitroditolyl sulphide (Kenner and Parkin, T., 1920, **117**, 855). In such cases, therefore, the choice lies between the use of alcoholic ammonia and of stannous chloride, and the following considerations suggested to us the possibility that different results would be obtained by the two processes.

It seems not unreasonable to assume that the reduction of a nitro-group is preceded by the formation of an additive compound of the nitro-compound with a molecule of hydrogen or of the reducing agent:

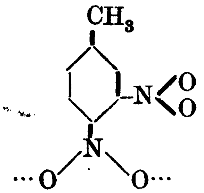
$$R\cdot NO_2+H_2 \longrightarrow R\cdot NO_2\ldots\ldots H_2 \longrightarrow R\cdot NO+H_2O$$

or

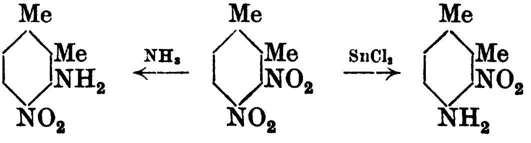
$$R\cdot NO_2+SnCl_2 \longrightarrow R\cdot NO_2\ldots\ldots SnCl_2 \longrightarrow R\cdot NO+SnOCl_2.$$

If this be premised, it would be expected that, of two nitro-groups, that one would suffer preferential reduction which is the more liable to form the necessary additive product. It will be recollected, however, that in previous papers of this series (T., 1914, **105**, 2717; 1920, **117**, 852) the explanation of the replacement of a substituent rendered mobile by a nitro-group is based on the assumption that the first stage consists in the formation of an additive compound through the nitro-group with the reagent employed, and hence that of two nitro-groups exposed to the action of alcoholic ammonia or similar reagents, that one will suffer displacement which is the less liable to form the preliminary additive product. It would therefore appear that, of two nitro-groups, that which suffers replacement under the influence of alcoholic ammonia or of sodium methoxide will be the more resistant to reduction.

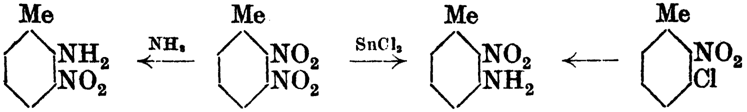
In this connexion, it is perhaps worth while to note that, for instance, the influence of the methyl group in determining the greater mobility of the 3- than the 4-nitro-group in 3 : 4-dinitrotoluene, as foreseen by the application of Flürscheim's hypothesis, would also be expected to render the 4-nitro-group more able to form additive compounds :



The action of ammonia and sodium methoxide on the dinitrotoluenes had already been investigated (Kenner and Parkin, *loc. cit.*), and it was therefore decided to submit these to partial reduction by means of stannous chloride and hydrochloric acid. The conditions employed were those which had been successfully applied by Crossley and Wren to the case of 3 : 4-dinitro-*o*-xylene, from which 3-nitro-*o*-4-xylidine was obtained, with indications of the formation of the isomeric 4-nitro-*o*-3-xylidine (T., 1911, **99**, 2342) :



We were enabled, by the kindness of Professor Crossley in supplying us with material, to supplement this result, and to show that 4-nitro-*o*-3-xylidine is obtained almost quantitatively by the action of alcoholic ammonia. Similarly, 2 : 3-dinitrotoluene, which is converted into 3-nitro-*o*-toluidine by the treatment with alcoholic ammonia, gives almost pure 2-*nitro*-m-*toluidine*, m. p. 107°, when reduced by stannous chloride:



The new base, which is deep red in colour, and is easily acetylated, has also been obtained by the action of ammonia on 3-chloro-2-nitrotoluene. This reaction takes place with considerable difficulty, doubtless owing to steric hindrance to the formation of the necessary preliminary additive product with the nitro-group.

It is probably safe to predict that, in compounds of this type, one or other of the nitro-groups may be replaced at will by suitable choice of the reagent to be employed, a possibility which may well be useful for synthetic purposes, since, in general, at present no other means is known by which the two isomerides may be obtained. It is fortunate from this point of view that the same difficulty does not exist in the cases of the nitroamines derived from 3 : 4- and 2 : 5-dinitrotoluenes. The former, from which almost pure 4-nitro-*m*-toluidine was obtained by treatment with alcoholic ammonia, when reduced with stannous chloride, gives a mixture of the two possible isomerides in almost equal proportions. From 2 : 5-dinitrotoluene, the product of the action of ammonia contained 88 per cent. of 5-nitro-*o*-toluidine, with 12 per cent. of 6-nitro-*m*-toluidine, whilst the proportions resulting from reduction by stannous chloride were 68 : 32.

A closer scrutiny of the reasoning employed above shows that a complete reversal of the results of the action of ammonia by that of stannous chloride is only to be expected if the nature of the additive product is similar, and if the ratio of its velocity of formation to that of its transformation is comparable, in the two cases. The former condition is very probably fulfilled, but observation shows that the latter is not satisfied. Thus, when a solution of stannous chloride in alcoholic hydrochloric acid is added to a suspension of a dinitro-compound in alcohol, there is a considerable development of colour, and the material at once passes into solution, indicating the immediate formation of an additive compound with stannous chloride. If the compounds thus produced are stable, as they may be in presence of the excess of stannous chloride employed, the relative proportions in which the two nitro-groups are reduced will depend chiefly on their relative tendencies to form the additive compound, as already discussed. The formation of the compounds with ammonia is not instantaneous, and is reversible, since complete solution does not occur when the nitro-compounds are mixed with this reagent, and the increased depth of colour produced by heat diminishes again on cooling. Such circumstances are much more favourable to considerable preponderance of one product over the other. The almost complete contrast nevertheless observed in the case of 2 : 3-dinitrotoluene and similar compounds must be ascribed to strong steric influences, the effect of which in each case is almost completely to inhibit one of the alternative courses of the reaction. The exact evaluation of the various factors referred to is hardly possible at present, and it is probably for this reason that the explanation so outlined would scarcely lead one to anticipate the formation of the two possible derivatives in equal proportions by the action of stannous chloride on 3 : 4-dinitrotoluene. Nevertheless, it suggests that the experimental results are not necessarily at variance with the theoretical considerations which suggested them.

EXPERIMENTAL.

Action of Ammonia on 3 : 4-Dinitro-o-xylene.

The dinitro-compound (1 gram) was heated with ammonia solution (2·5 c.c.; D 0·880) and methyl alcohol (13·5 c.c.) for two successive periods of eight hours at 160°, to ensure completion of the reaction, although this was probably achieved in eight hours. On cooling, the base (0·55 gram) separated in red scales, m. p. 118·5°, in complete agreement with the account given of 4-nitro-*o*-3-xylidine by Noelting, Braun, and Thesmar (*Ber.*, 1901, **34**, 2244). A further quantity (0·2 gram) of the base, m. p. 110—113°, and finally a small quantity of oily material, which only slowly solidified, were obtained from the solution. The isomeric base crystallises in needles, but no sign of these was observed.

Reduction of the Dinitrotoluenes by Stannous Chloride and Hydrochloric Acid.

2 : 3-*Dinitrotoluene.*—When a solution of stannous chloride (21·5 grams) in absolute alcohol (107 c.c.), previously saturated with dry hydrogen chloride, was added to a suspension of 2 : 3-dinitrotoluene (5 grams) in alcohol (40 c.c.) at 7°, complete solution at once occurred. After twelve hours, alcohol (120 c.c.) was removed by distillation, and the residue poured into water. The precipitate was extracted with concentrated hydrochloric acid in order to separate unreduced nitro-compound (1·3 grams) from nitroamine (1·3 grams), m. p. 90—105°, which was recovered from solution

by precipitation with ammonia. The original acid liquor yielded a further quantity (1·4 grams) on extraction with ether, and in addition a small amount of diamino-compound, weighed as hydrochloride (0·8 gram), after treatment with excess of alkali. A mixture of the crude nitroamine with 3-nitro-*o*-toluidine melted at 70°. The crude base was purified by crystallisation from a mixture of light petroleum and benzene, from which it separated in deep red prisms, m. p. 107—108°. The same product, when first obtained by reduction under somewhat different conditions (Kenner and Parkin, *loc. cit.*), was mistaken for an azo-compound, since a product obtained by Limpricht (*loc. cit.*) had been considered to be *2-nitro-*m*-toluidine* (Noelting and Stoecklin, *loc. cit.*), and is described as forming pale yellow needles, m. p. 53°. There can be little doubt, however, that this constitution must be assigned to the compound now described, since, in addition to its basic properties, evidenced by its method of isolation, it at once reacts with acetyl chloride and acetic anhydride and the analysis previously communicated is in better agreement with this view. *2-Nitroaceto-*m*-toluidide* separates from a mixture of light petroleum and benzene in transparent prisms, m. p. 126°.

The constitution of 2-nitro-*m*-toluidine was also determined by its synthesis from 3-chloro-2-nitrotoluene. This compound was obtained from 2 : 4-dinitrotoluene according to the directions of Brand and Zöller (*Ber.*, 1907, **40**, 3333), with the modification that the preparation of 2-nitro-4-hydroxylaminotoluene was carried out by means of zinc dust and ammonium chloride, as prescribed by Bamberger and Baudisch in the case of *p*-chlorophenylhydroxylamine (*Ber.*, 1909, **42**, 3581). The melting points of the hydroxylamino-compound and of 3-chloro-2-nitro-*p*-toluidine were respectively observed as 106° and 67—68°, in place of 99° and 63° quoted by Brand and Zöller.

3-Chloro-2-nitrotoluene (2 grams) was heated with concentrated ammonia solution (3 grams; D 0·880) at 200° for eight hours. The desired base was separated from unchanged material by extraction with concentrated hydrochloric acid, and reprecipitated with ammonia. After crystallisation from light petroleum, it melted at 106°, and caused no depression in melting point of the base obtained from 2 : 3-dinitrotoluene.

3 : 4-*Dinitrotoluene.*—A suspension of the dinitro-compound (10 grams) in alcohol (80 c.c.) was treated with a solution of stannous chloride (36 grams) in absolute alcohol (180 c.c.) previously saturated with dry hydrogen chloride. The mixture was worked up in the manner already described for 2 : 3-dinitrotoluene, and yielded unchanged dinitro-compound (5·8 grams), diamine hydrochloride

(0·5 gram), and crude nitroamine (3·5 grams), f. p. 50°. Since the eutectic point for a mixture of 4-nitro-*m*-toluidine and 3-nitro-*p*-toluidine is 70°, it was evident that some impurity was present. The base was therefore purified by washing its solution in ether with dilute sodium hydroxide solution, and finally by solution in light petroleum, a certain amount of tarry material being thus eliminated. The base thus obtained showed f. p. 70°, corresponding with a mixture of the two isomerides containing 48 per cent. of 4-nitro-*m*-toluidine. The melting point was considerably raised by admixture with an approximately equal quantity of either of the two isomerides.

2 : 5-*Dinitrotoluene*.—A suspension of the dinitro-compound (5 grams) in alcohol (40 c.c.), after treatment with a solution of stannous chloride (18 grams) in absolute alcohol (90 c.c.) saturated with dry hydrogen chloride, yielded unchanged dinitrotoluene (0·5 gram), diamine hydrochloride (0·65 gram), and nitroamine (3·5 grams), f. p. 97°. This corresponds with a mixture of 62 per cent. of 5-nitro-*o*-toluidine with 38 per cent. of 6-nitro-*m*-toluidine. After crystallisation from light petroleum, the melting point was 110°, and this was raised by addition of 5-nitro-*o*-toluidine, but depressed by addition of 6-nitro-*m*-toluidine.

In conclusion, the authors wish to express their thanks to the Advisory Council for Scientific and Industrial Research for a grant which has enabled one of them to take part in this work, to The British Dyestuffs Corporation for supplies of material, and to the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

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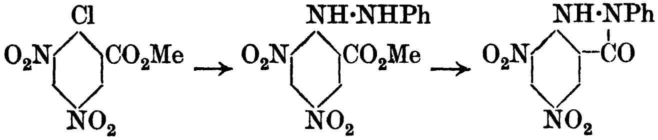
CXIV.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part IV. The Condensation of Ethyl* 3- *and* 5-*Nitro*-2-*chlorobenzoates with Hydrazines.*

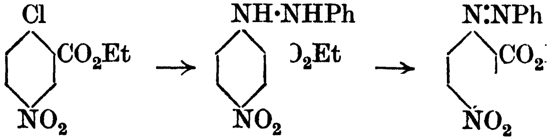
By JAMES KENNER and ERNEST WITHAM.

SOME years ago it was shown that 5 : 7-dinitro-3-keto-1 : 3-dihydroindazole was obtained as the direct product of the action of hydrazine on methyl 2-chloro-3 : 5-dinitrobenzoate, and that even when phenylhydrazine was used the intermediate 2 : 4-dinitro-6-carbomethoxyhydrazobenzene was only isolated under certain conditions, and readily underwent internal condensation with formation of the ketodihydroindazole derivative (Kenner, T., 1914, **105**, 2732):



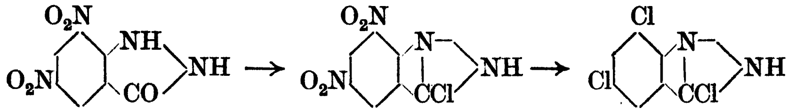
The last reaction took place so readily that it was not possible to obtain definite evidence of the position of the phenyl group in the side-chain by oxidation with mercuric oxide or by condensation with benzaldehyde. Another product, which was considered to be the phenylhydrazide of the above intermediate product, was sufficiently stable for such purposes, but did not react with either of the reagents named. In the hope of obtaining more definite evidence as to the formulæ of the compounds in question, it was decided to study the behaviour of the esters of 3- and 5-nitro-2-chlorobenzoic acids respectively towards hydrazine and its phenyl derivative.

As had been anticipated, the esters in question were much less reactive than the corresponding dinitro-derivative, and the product of their interaction with hydrazine was in each case a mixture of a nitro-2-carbethoxyphenylhydrazine with the indazole derivative resulting from its internal condensation. Similarly, with phenylhydrazine in each case the phenyl derivatives of these compounds were obtained. The intermediate product from ethyl 2-chloro-5-nitrobenzoate was easily oxidised by yellow mercuric oxide to an azo-compound and was therefore 4-nitro-2-carbethoxyhydrazobenzene:



Further, by treatment with sodium hydroxide, it was converted into 5-nitro-3-keto-2-phenyl-1 : 3-dihydroindazole. These reactions served to confirm the formulæ assigned to the compounds previously described. The failure to oxidise the hydrazobenzene derivative of that series was apparently due to steric causes, since it was found that the corresponding derivative from ethyl 2-chloro-3-nitrobenzoate was also quite stable towards yellow mercuric oxide.

In the previous paper, it was shown that the chloroindazoles obtained by treatment of the above-mentioned ketodihydroindazoles with phosphoryl chloride at 140° suffered replacement of their nitro-groups by chlorine atoms when the reaction was carried out at 170° :



This reaction did not, however, occur in the case of the chloroindazoles derived from ethyl 2-chloro-5-nitrobenzoate.

EXPERIMENTAL.

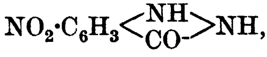
Action of Hydrazine Hydrate on Ethyl 2-Chloro-5-nitrobenzoate.

A mixture of hydrazine hydrate (12 grams) with a solution of ethyl 2-chloro-5-nitrobenzoate (20 grams) in absolute alcohol (100 c.c.) was heated on the water-bath. Crystallisation ensued after about twenty minutes, and after a further fifteen minutes the mixture was cooled and filtered.

4-*Nitro-2-carbethoxyphenylhydrazine*, $NO_2\cdot C_6H_3(CO_2Et)\cdot NH\cdot NH_2$, was separated by washing the crystals with hot water until they were free from the purple salt of the accompanying indazole derivative described below. By crystallisation from alcohol, it was obtained in yellow needles, m. p. 172° (Found : $N=18\cdot 9$. $C_9H_{11}O_4N_3$ requires $N=18\cdot 70$ per cent.).

Its *acetyl* derivative was immediately produced by the action of acetic anhydride, and separated from glacial acetic acid in faintly green needles, m. p. 191·5° (Found : $N=16\cdot 15$. $C_{11}H_{13}O_5N_3$ requires $N=15\cdot 8$ per cent.).

Benzaldehyde 4-*nitro-2-carbethoxyphenylhydrazone* forms prismatic needles, m. p. 165—166° (Found : $N=13\cdot 66$. $C_{16}H_{15}O_4N_3$ requires $N=13\cdot 42$ per cent.).



5-*Nitro-3-keto-*1 : 3-*dihydroindazole*, $NO_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{NH}{CO}{>}NH$, was obtained by acidification of the filtrate from the above reaction. It is sparingly soluble in alcohol, and was purified by crystallisation from glacial acetic acid, and so obtained in small reddish-brown aggregates of prisms, m. p. 273° with decomposition (Found : $N=23\cdot 55$. $C_7H_5O_3N_3$ requires $N=23\cdot 47$ per cent.).

Its *acetyl* derivative was at once obtained by the addition of a drop of sulphuric acid to a mixture of the compound with acetic anhydride. After crystallisation from glacial acetic acid, it formed small, faintly yellow prisms, m. p. 239° (Found: N=19·03. $C_9H_7O_4N_3$ requires N=19·00 per cent.).

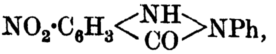
The *monosodium* salt, prepared by triturating 5-nitro-3-keto-1 : 3-dihydroindazole (2 grams) with 2*N*-sodium hydroxide solution (8 c.c.), separated from the solution on the addition of alcohol (5 c.c.) as a dark orange-red, crystalline powder (Found: after drying at 130°, Na=11·32, 11·41. $C_7H_4O_3N_3Na$ requires Na=11·44 per cent.).

5-*Amino*-3-*keto*-1 : 3-*dihydroindazole* was prepared by heating the nitro-compound (2 grams) with tin (5 grams) and hydrochloric acid (45 c.c.). From the double tin salt, which separated on cooling, the *hydrochloride* of the base was isolated in the usual manner as colourless needles, m. p. 286° (decomp.), which assumed a slate colour on keeping (Found: N=18·63. $C_7H_7ON_3,2HCl$ requires N=18·92 per cent.).

Action of Phenylhydrazine on Ethyl 2-Chloro-5-nitrobenzoate.

A solution of the ester (15 grams) in alcohol (66 c.c.) was warmed on the water-bath with phenylhydrazine (23 grams). After eight hours, the mixture began to bump; it was therefore cooled, and filtered. A further quantity of material was obtained by renewed heating of the liquor. The crude product was washed with hot dilute hydrochloric acid to remove phenylhydrazine hydrochloride, and crystallised from alcohol. It formed yellow prisms, m. p. 133° (Found: N=14·16. $C_{15}H_{15}O_4N_3$ requires N=13·94 per cent.). The compound was therefore 4-*nitro*-2-*carbethoxyhydrazobenzene*, $NO_2\cdot C_6H_3(CO_2Et)\cdot NH\cdot NHPh$. In conformity with this formula, a solution of the compound (2·9 grams) in alcohol (35 c.c.) was rapidly oxidised by yellow mercuric oxide (4 grams). From the solution, 4-*nitro*-2-*carbethoxyazobenzene* (2·4 grams) was obtained in groups of red, hexagonal plates, m. p. 70—71° (Found: N=14·29. $C_{15}H_{13}O_4N_3$ requires N=14·05 per cent.).

5-*Nitro*-3-*keto*-2-*phenyl*-1 : 3-*dihydroindazole*,

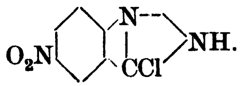


$$NO_2\cdot C_6H_3{<}{\substack{NH\\CO}}{>}NPh,$$

was not produced in the above reaction, but was prepared by boiling 4-nitro-2-carbethoxyhydrazobenzene (8 grams) with *N*/2-sodium hydroxide solution (200 c.c.) for five minutes. The precipitate obtained on acidification separated from glacial acetic acid in faintly green needles, m. p. 270—273° with decomposition (Found: N=16·26. $C_{13}H_9O_3N_3$ requires N=16·47 per cent.).

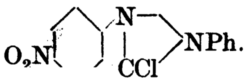
The *monosodium* salt, prepared as described in the case of the above nitroketodihydroindazole, was obtained as a dark brownish-red, crystalline precipitate (Found: after drying at 130°, Na=7·21, 7·11. $C_{13}H_8O_3N_3Na,C_2H_6O$ requires Na=7·12 per cent.).

3-*Chloro*-5-*nitroindazole*,



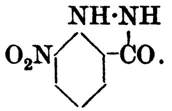
This compound was prepared by heating 5-nitro-3-keto-1 : 3-dihydroindazole (5 grams) with phosphoryl chloride (35 grams) for five hours at 120—130°. The product was isolated in the usual way, and crystallised from glacial acetic acid. In this way, faintly yellow needles, m. p. 210—211°, were obtained (Found: N=21·39. $C_7H_4O_2N_3Cl$ requires N=21·37 per cent.).

3-*Chloro*-5-*nitro*-2-*phenylindazole*,



This compound, prepared in an analogous manner to the preceding one, formed small prisms, m. p. 165° (Found: N=15·57. $C_{13}H_8O_2N_3Cl$ requires N=15·35 per cent.).

7-*Nitro*-3-*keto*-1 : 3-*dihydroindazole*,



A solution of ethyl 2-chloro-3-nitrobenzoate (30 grams) in alcohol (500 c.c.) was heated with an aqueous solution (150 c.c.) of hydrazine hydrate (30 grams) for three and a half hours on the water-bath. Alcohol was then removed by distillation, and the solution diluted with water, and acidified after filtration from a very slight residue. The yellow product (23 grams) separated from glacial acetic acid in copper-coloured plates with a blue reflex, m. p. 290° (decomp.) (Found: N=23·33. $C_7H_5O_3N_3$ requires N=23·46 per cent.).

The *acetyl* derivative forms brown needles, m. p. 196—197°.

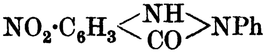
The *monosodium* salt was obtained in the usual manner (Found: after drying at 140°, Na=11·55. $C_7H_4O_3N_3Na$ requires Na=11·55 per cent.).

Action of Phenylhydrazine on Ethyl 2-*Chloro*-3-*nitrobenzoate*.

The ester (4·5 grams) was heated at 100° with phenylhydrazine (7 grams) and alcohol (20 c.c.) for thirty hours, after which the alcohol was removed by evaporation. The residue, after treatment with dilute sodium hydroxide solution, was extracted. The extract, after being washed with dilute hydrochloric acid to remove phenylhydrazine, on evaporation yielded a mass of crystals (1·6 grams), which was purified by crystallisation.

2-*Nitro*-6-*carbethoxyhydrazobenzene*, $NO_2\cdot C_6H_3(CO_2Et)\cdot NH\cdot NHPh$, prepared in this manner, forms clusters of greenish-yellow needles, m. p. 119° (Found: N=14·45. $C_{15}H_{15}O_4N_3$ requires N=14·05 per cent.). It was recovered unchanged after boiling in alcoholic solution with yellow mercuric oxide for twelve hours; there was no development of colour in the solution, and the oxide showed no signs of blackening.

7-*Nitro*-3-*keto*-2-*phenyl*-1 : 3-*dihydroindazole*,



$$NO_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{NH}{CO}{>}NPh$$

(3·5 grams), was precipitated on acidification of the sodium hydroxide solution referred to above, and obtained in minute, greenish-yellow prisms, m. p. 185°, by crystallisation (Found: N=16·12. $C_{13}H_9O_3N_3$ requires N=16·47 per cent.).

The *monosodium* salt gives a purple solution, and has a noticeable tendency to sublime at 140° (Found: after drying at 140°, Na=7·47. $C_{13}H_8O_3N_3Na,C_2H_6O$ requires Na=7·12 per cent.).

The authors have pleasure in expressing grateful acknowledgment of a grant from the Research Fund of the Chemical Society towards the expenses of this investigation.

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CXV.—*Researches on Residual Affinity and Co-ordination. Part V. Gallium Acetylacetone and its Analogues.*

By GILBERT T. MORGAN AND HARRY DUGALD KEITH DREW.

THE third vertical series of the periodic classification of the elements furnishes an example of two related natural families, the respective members of which show a marked tendency to yield acetylacetone derivatives. Apart from a few acetylacetones of the least common of the rare-earth metals, the only missing member of the series is *gallium acetylacetone*, which is now described in the present communication.

The starting-point in this research was 0·12 gram of metallic gallium, originally prepared by Lecoq de Boisbaudran and pre sented by him to Sir Walter Hartley and Dr. J. H. Pollok. On the death of the latter, this precious metal passed into the possession of one of us (G. T. M.) and was employed in our earlier experiments, which, however, were much restricted in scope by the small amount of material available. At this stage 2 grams of gallium hydroxide were generously placed at our disposal by Professor C. James, to whom our best thanks are due.

A comparative study showed that the French and American samples gave rise to identically the same acetylacetone derivative, so that with the larger specimen we were able to confirm the results obtained with the smaller.

Gallium acetylacetone is most conveniently prepared by the action of acetylacetone on freshly precipitated gallium hydroxide, a method which is also quite efficacious in the production of aluminium and indium acetylacetones. The yields in the three cases are practically quantitative.

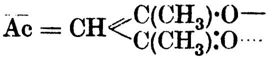
The following tabulation summarises the data obtained by a comparative study of the acetylacetones of these closely allied metals.

	Acetylacetones of		
Properties.	Aluminium, $Al(C_5H_7O_2)_3$	Gallium, $Ga(C_5H_7O_2)_3$	Indium, $In(C_5H_7O_2)_3$
Molecular weight (1) calculated	324	367	412
(2) determined (i) cryoscopically	323	342	404
(ii) ebullioscopically	333	353	414
All sublime at 140° under 10 mm. pressure	Very slight residue	Slight residue	Considerable residue
Melting point	192—194°	194—195°	186—187°
Reaction with aquo-alcoholic ferric chloride	Very slow development of red coloration	More rapid development of red coloration	Most rapid development of coloration
Crystalline form	Monoclinic	Dimorphous α-Form monoclinic, isomorphous with the Al compound. β-Form orthorhombic, isomorphous with the β-form of the In compound.	Dimorphous β-Form orthorhombic, like the β-form of the Ga compound. γ-Form orthorhombic, but quite different from the β-form.

These data show that in solution the three compounds have the general molecular formula RAc_3, (compare Chabrié and Rengade, *Compt. rend.*, 1900, **131**, 1300; 1901, **132**, 472).

The three metallic acetylacetones are not equally stable and resistant to chemical reagents, as is shown by their behaviour in an exhausted sublimation chamber and by the speed of reaction with ferric chloride. In addition to the foregoing properties, gallium acetylacetone justifies its position between the acetyl acetones of aluminium and indium by a manifestation of dimorphism. In one of these forms it is monoclinic and isomorphous with aluminium acetylacetone. In the other form, it is orthorhombic and isomorphous with one of two orthorhombic forms of indium acetylacetone.

With the completion of this series of metallic acetylacetones derived from the elements of the boron–aluminium family, it becomes of interest to note the gradual change of constitution and properties as the third periodic series of elements is ascended from boron to thallium, $\bar{\mathrm{A}}\mathrm{c}$ being the univalent chelate complex.



$$\bar{\mathrm{A}}\mathrm{c} = \mathrm{CH}{<}\genfrac{}{}{0pt}{}{\mathrm{C(CH_3)\cdot O-}}{\mathrm{C(CH_3):O\cdots}}$$

$$\begin{array}{cccccccc} & \mathrm{Al\bar{A}c_3} & & \mathbf{Ga\bar{A}c_3} & & \mathrm{In\bar{A}c_3} & & \mathrm{Tl\bar{A}c} \\ [\mathrm{B\bar{A}c_2}]\mathrm{Cl} & & \mathrm{Sc\bar{A}c_3} & & \mathrm{Y\bar{A}c_3} & & \mathrm{Pr_2\bar{A}c_6} & \end{array}$$

In these acetylacetone derivatives, all the elements except the first and the last have a co-ordination number 6. With boron, this number is 4, whereas with univalent thallium it has fallen to 2. Thallous acetylacetone, however, shows signs of unsaturation, indicated by the formation of an additive compound with carbon disulphide (Kurowski, *Ber.*, 1900, **43**, 1079). The complete saturation of the principal and supplementary valencies is manifested in the cases of aluminium, gallium, and indium by the monomeric molecular weight of the acetylacetones and by the absence of ammonia additive products of these compounds. This saturation of the chemical affinity is also shown with the rare-earth metals of low atomic weight. Scandium and yttrium acetylacetones have the simple molecular formula in organic solvents, and do not furnish additive compounds with ammonia (T., 1914, **105**, 189). In the main group of rare-earth metals, however, the acetylacetones exhibit twofold association in organic solvents and give rise to additive compounds with ammonia and organic amines.

EXPERIMENTAL.

Preparation of the Acetylacetones of the Gallium Group.

1. Of the anhydrous chlorides of aluminium, gallium, and indium, only the first interacted with acetylacetone in chloroform solution, giving a quantitative yield of aluminium acetylacetone (m. p. 191—

193°). The negative result with the other two compounds may, however, be due to the decreasing solubility of the chlorides in this solvent as the atomic weight increases.

2. Interaction of acetylacetone and the precipitated hydroxides of these three metals proceeded very slowly, and the yields were unfavourable.

3. The optimum result was obtained by refluxing an aqueous solution of the metallic nitrate with a slight excess of acetylacetone, ammonia being added little by little so that the nascent metallic hydroxide was attacked forthwith by the organic reagent. In this way aluminium acetylacetone was obtained quite pure and in quantitative yield, so that the process affords a gravimetric method of estimating aluminium.

The metallic gallium employed in the earlier experiments was prepared by Lecoq de Boisbaudran from a Pyrenean source; it melted within the limits 30—35°, but it has since been shown that an accurate determination of the melting point of gallium cannot be obtained with small quantities of the metal. Richards and Boyer, who used 10 grams of the metal, found its melting point to be 29·75° (*J. Amer. Chem. Soc.*, 1920, **43**, 274).

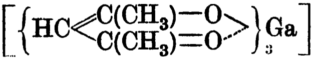
The Pyrenean gallium was warmed in a stream of dry chlorine; the colourless gallium trichloride, which was easily fusible and vaporisable, was heated in a current of dry carbon dioxide to remove excess of the halogen. The trichloride was employed unsuccessfully with acetylacetone in chloroform solution and was recovered as the nitrate (after evaporation) from the syrupy residue by heating with concentrated nitric acid, the excess of acid being removed by warm, dry air.

The crystalline nitrate, dissolved in water and neutralised with ammonia until a faint turbidity appeared, was refluxed with 0·9 gram of acetylacetone, dilute ammonia (1 c.c. of strong ammonia : 10 c.c. of water) being slowly added. Each drop produced a turbidity which disappeared immediately, and was replaced by a crystalline precipitate of gallium acetylacetone. After cessation of the turbidity, the solution was heated for thirty minutes at 100° and then cooled. The product, after crystallisation from benzene, melted at 192—193° (yield about 70 per cent. of the calculated amount).

The foregoing preparation was repeated on 0·42 gram of gallium hydroxide of American origin, and 1·16 grams of gallium acetylacetone were obtained, or 91 per cent. of the theory. Another experiment gave a 93 per cent. yield.

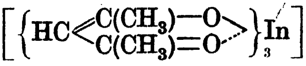
After crystallisation from acetone, the product melted sharply at 194°, and a mixed melting point with the sample of French origin gave 192—194°. The recrystallised product was analysed (Found: C=49·08; H=6·00; Ga=18·86. $C_{15}H_{21}O_6Ga$ requires C=49·02; H=5·77; Ga=19·08 per cent.).

The gallium oxide recovered from these estimations was a pure white powder insoluble in hot, concentrated nitric acid; its solubility was regained by fusion with pure potassium hydrogen sulphate.



$$\left[\left\{\mathrm{HC}\!<\!\begin{matrix}\mathrm{C(CH_3)-O}\\ \mathrm{C(CH_3)=O}\end{matrix}\!>\right\}_3\mathrm{Ga}\right]$$

(I.)



$$\left[\left\{\mathrm{HC}\!<\!\begin{matrix}\mathrm{C(CH_3)-O}\\ \mathrm{C(CH_3)=O}\end{matrix}\!>\right\}_3\mathrm{In}\right]$$

(II.)

Gallium acetylacetone (I), which was almost insoluble in water and slightly soluble in cold ether or alcohol, dissolved readily in chloroform or acetone, separating from the former in colourless, acicular forms, and from the latter in transparent, tabular crystals. It was readily soluble in cold benzene. The purest specimen, obtained by crystallisation from acetone and subsequent sublimation at 170° under reduced pressure, melted at 194—195°. The sublimation of gallium acetylacetone, even under 10 mm. pressure, was accompanied by a slight decomposition, and it was not found possible to determine its vapour density by Victor Meyer's method. The molecular weight was, however, determined cryoscopically in Kahlbaum's pure benzene. The numbers obtained for concentrations varying from 2·15 to 2·77 grams per 100 grams of solvent were: specimen from French gallium, M=340; from American gallium, M=343, 344, 337, 346. Ebullioscopic determinations in the same solvent gave, for the sample from American gallium, M=353. $Ga\bar{A}c_3$ requires M=367. Measurable crystals of the two forms (α- and β-) of gallium acetylacetone were obtained by crystallisation from acetone. From cold chloroform, the compound separated in transparent needles, which rapidly fell to powder.

Indium Acetylacetone (II).—Metallic indium (Kahlbaum's preparation) was dissolved in strong nitric acid, the solution concentrated, and the crystalline nitrate dissolved in water and treated with acetylacetone and ammonia as in the case of the gallium compound. The freshly-prepared indium compound consisted of large, colourless crystals, which fell to powder when removed from the aqueous mother-liquor. On crystallisation from cold acetone, indium acetylacetone separated at first in colourless needles, which fell to powder on keeping; it melted sharply at 186°, sublimed under reduced pressure, but left a considerable residue. It was readily soluble in benzene, but only moderately soluble in alcohol, and almost insoluble in water. The sublimed product melted at 186—

187°, but on account of its imperfect volatility the vapour density of indium acetylacetone could not be determined by Victor Meyer's method. Its molecular weight was, however, obtained in benzene solution.

The cryoscopic method (w/W=1·6/100) gave M=404 and the ebullioscopic process (w/W=3·2/100) indicated M=414. $\mathrm{In\overline{Ac}_3}$ requires M=412. Measurable crystals of indium acetylacetone were obtained by slow crystallisation from warm acetone.

Aluminium acetylacetone, prepared from aluminium nitrate, was compared with its gallium and indium analogues. When sublimed, it left only a very slight residue; its vapour density by Victor Meyer's method approximated to a molecular weight of 300. The cryoscopic and ebullioscopic determinations gave M=323 and 333 respectively; $\mathrm{Al\overline{Ac}_3}$ requires M=324.

The three acetylacetones, when taken in pairs, gave the following mixed melting points, which show comparatively slight depression :

$\mathrm{Al\overline{Ac}_3-Ga\overline{Ac}_3}$	$\mathrm{Al\overline{Ac}_3-In\overline{Ac}_3}$	$\mathrm{Ga\overline{Ac}_3-In\overline{Ac}_3}$
189—192°	178—180°	183—184°

Aluminium acetylacetone separated from chloroform in massive, colourless crystals, which fell to powder on keeping in the air. A more permanent preparation, employed in the following crystallographic measurements, was obtained by crystallisation from acetone.

Report on the Crystallographic Characteristics of the Acetylacetone Derivatives of Aluminium, Gallium, Indium, Scandium, and Iron.

The following report has been contributed by Mr. T. V. Barker, who kindly undertook the crystallographic examination of some of our preparations.

The acetylacetones of aluminium and iron have been previously described by von Lang (*Sitzungsber. Akad. Wiss. Wien*, 1899 [*Math.-Phys. Klasse*], **108**, 1166), whose results failed to reveal any close similarity, for the first compound crystallises in the monoclinic, and the second in the orthorhombic system. Later researches by Jaeger (*Rec. trav. chim.*, 1914, **33**, 388) on the scandium and indium derivatives showed that they are isomorphous with the iron compound described by von Lang. The present investigation has led to the interesting result that both the gallium and indium compounds are dimorphous, and that the whole series of five compounds are really closely related to each other, since they collectively present a case of isotrimorphism. This relationship can be best described in the form of a table.

Table of Crystallographic Elements of the Tervalent Metallic Acetylacetones.

(1) Aluminium; monoclinic, $a : b : c = 1{\cdot}901 : 1 : 1{\cdot}111$, $\beta = 98° 54'$	Isomorphous
(2) Gallium (α-form); monoclinic, $a : b : c = 1{\cdot}834 : 1 : 1{\cdot}069$, $\beta = 99° 12'$	
(3) Gallium (β-form); orthorhombic, $a : b : c = 0{\cdot}6314 : 1 : 1{\cdot}253$	Isomorphous
(4) Indium (β-form); orthorhombic, $a : b : c = 0{\cdot}6168 : 1 : 1{\cdot}291$	
(5) Indium (γ-form : Jaeger); orthorhombic, $a : b : c = 0{\cdot}5593 : 1 : ?$	Isomorphous
(6) Scandium (γ-form : Jaeger); orthorhombic, $a : b : c = 0{\cdot}5621 : 1 : ?$	
(7) Iron (γ-form : von Lang); orthorhombic, $a : b : c = 0{\cdot}5689 : 1 : 1{\cdot}222$	

It must here be added that indium acetylacetone crystallises in a third, unstable modification as fine needles, which, unfortunately, are not suitable for a full crystallographic investigation; but since they exhibit oblique extinction, they can scarcely be isomorphous with aluminium acetylacetone.

In view of the possibility that the molecular configuration of this series of compounds is of an enantiomorphous nature, it is at least conceivable that the appearance of gallium and indium acetylacetones in more than one form is due to an alternative separation in optically active and racemic forms; but as no hemihedral facets have been observed, no mechanical separation was possible. Attempts to grow individual crystals sufficiently large for a polarimetric examination are now in progress.

Aluminium Acetylacetone.—The crystals previously examined by von Lang were of the general habit shown in Fig. 1 in so far as the forms $a\{100\}$, $c\{001\}$, and $m\{110\}$ are concerned. On one occasion he also observed two additional facets, to which he allotted the indices $(\bar{1}01)$ and $(\bar{3}01)$, but the reflections were so poor that he was not satisfied that they correspond with real faces. The crystals sent to Oxford for examination generally exhibited the simple combination a, c, and m, but a face $r(\bar{1}01)$ was observed on three crystals. The values for the angle $a'r = (100 : \bar{1}01)$ were respectively 65° 55′, 66° 36′, and 66° 46′. If the mean value 66° 26′ be adopted in lieu of von Lang's questionable single value 62° 24′, the crystal elements become $a : b : c = 1{\cdot}901 : 1 : 1{\cdot}111$, $\beta = 98° 54'$. These values present a very close approximation to those of the isomorphous gallium derivative of acetylacetone.

Gallium Acetylacetone.—Two crops of this substance, in addition to one or two isolated crystals, were received for examination. One crop wholly consisted of orthorhombic crystals; the other was a mixture of the monoclinic and orthorhombic forms, which could be picked apart after a little practice. The two forms have the same faintly yellow colour and are occasionally so similar as to be almost indistinguishable, except by measurement.

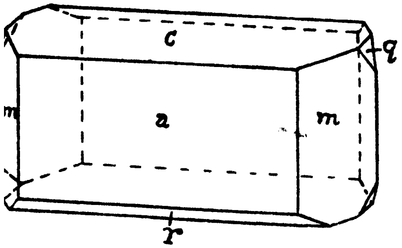
The monoclinic form generally only presents the simple combination $a\{100\}$, $m\{110\}$, and $c\{001\}$, but two crystals were fortunately found, one exhibiting the additional forms *r*{$\bar{1}$01} and *q*{021} shown in Fig. 1, whilst the other exhibited *r* without *q*. The crystal elements are $a : b : c = 1{\cdot}834 : 1 : 1{\cdot}069$, $\beta = 99° 12'$. Following are the results obtained by adjusting the most highly developed pair of crystals about the zone *ac* :

	m(110)	*a*(100)	*c*(001)	*q*(021)	*r*($\bar{1}$01)
Azimuth (ϕ)	0° 0′	0° 0′	*80° 48′	80° 48′	*113° 12′
Polar distance (ρ)	*28 55	90 0	90 0	25 15(+6)	90 0

There is no marked cleavage. The optical properties are in accordance with monoclinic symmetry.

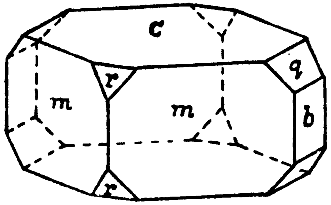
The orthorhombic form generally presents the simple combination *c*{100}, *m*{110}, and *b*{010}, but one crystal (of the general habit shown in Fig. 2, devoid of *r*) was observed, with the additional form *q*{011}. The mean results obtained from two crystals were :

FIG. 1.



Aluminium and gallium acetylacetones (monoclinic).

FIG. 2.



Gallium and indium acetylacetones (orthorhombic).

$bm = 57° 44'$, $mm = 64° 32'$, $cq = 51° 24'$; whence $a : b : c = 0{\cdot}6314 : 1 : 1{\cdot}253$. There is a perfect basal cleavage, normal to which is the negative acute bisectrix. The axial plane is *b*(010) with a wide angle and $\rho < v$. The birefringence is very strong.

Indium Acetylacetone.—The faint brownish-yellow crystals of this substance proved to be simple combinations of *c*{001}, *m*{110}, and *b*{010}, on the general lines of Fig. 2, but devoid of *q*{011} and *r*{101}. A single facet *r*(101) was, however, fortunately observed on one crystal, so that a complete set of crystal elements could be deduced. The mean results obtained from three crystals were : $bm = 58° 20'$, $mm = 63° 19'$, $cr = 64° 28'$; whence $a : b : c = 0{\cdot}6168 : 1 : 1{\cdot}291$. There is a fair cleavage parallel to the basal plane, and the optical properties are in every way similar to those of the orthorhombic form of gallium acetylacetone, with which it is obviously isomorphous. It must be mentioned that this modification is not identical with that observed by Jaeger, either in angles, cleavage, or optical properties.

As mentioned previously, the third "unstable form" of indium acetylacetone was not suitable for a goniometrical examination.

The authors desire to express their thanks to the Department of Scientific and Industrial Research for grants which have partly defrayed the expense of this investigation.

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CXVI.—*Researches on Residual Affinity and Co-ordination. Part VI. Selenodithionic Acid and its Metallic Salts.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

IN an earlier communication (T., 1920, **117**, 1461) it was shown that selenium acetylacetone reacted quantitatively with sodium or potassium hydrogen sulphite, giving rise to acetylacetone and the corresponding alkali selenodithionate :

$$[C_5H_6O_2{:}Se]_2+4R'HSO_3=2C_5H_8O_2+2Se(SO_3R')_2.$$

This reaction has been extended to the production of other metallic selenodithionates, and the *lithium*, *rubidium*, *cæsium*, and *ammonium* salts have now been prepared in a state of purity. The isolation of *barium selenodithionate* shows that the reaction is also applicable to the case of the metals of the alkaline earths. With sulphurous acid and selenium acetylacetone a similar double decomposition occurs, with the production of *selenodithionic acid* :

$$[C_5H_6O_2{:}Se]_2+4H_2SO_3=2C_5H_8O_2+2Se(SO_3H)_2.$$

This acid has not been obtained in a concentrated form, for, when its aqueous solution is evaporated at the ordinary temperature under reduced pressure, red selenium separates when a strength of approximately 50 per cent. (or 8*N*-) is reached. At higher concentrations, the aqueous solution deposits selenium and evolves sulphur dioxide, even at 0°. On treatment with aqueous thallous hydroxide, selenodithionic acid yields thallous selenide and sulphuric acid :

$$Se(SO_3H)_2+2TlOH=Tl_2Se+2H_2SO_4.$$

EXPERIMENTAL.

By a modification of the method formerly employed (*loc. cit.*) selenium acetylacetone was produced in considerably better yield, with a ready recovery of the by-product, chloroacetylacetone, in the form of its copper derivative.

Acetylacetone (4 mols.), dissolved in its own weight of anhydrous ether, was added slowly to finely divided selenium tetrachloride (2 mols.) suspended in an equal weight of ether. Considerable heat was generated and the mixture was maintained at about 0° by external cooling. The tetrachloride dissolved to an intensely red solution, evolving hydrogen chloride; the ether was then evaporated in a rapid stream of air, which passed through a series of wash bottles charged with an aqueous solution of copper and sodium acetates, from which pale green copper chloroacetylacetone separated (yield 75 per cent. of the calculated quantity). The residue, after removing the volatile solvent, consisted of pale yellow, crude selenium acetylacetone, which was purified by extraction with dry benzene in a Soxhlet apparatus (yield 87 per cent.). In this preparation ether may be replaced by cheaper benzene, but the evaporation takes considerably longer. An attempt to inhibit the formation of chloroacetylacetone as a by-product by the addition of elemental selenium to the tetrachloride was not successful, 94 per cent. of the free element being recovered.

Lithium selenodithionate, $Se(SO_3Li)_2,3H_2O$, an extremely soluble salt, was produced by adding seven grams of finely divided selenium acetylacetone to 5·2 grams of lithium sulphite, $Li_2SO_3,2H_2O$, in 45 c.c. of 2*N*-sulphurous acid. The mixture was shaken mechanically for one hour, selenium acetylacetone disappeared, the liquid was extracted repeatedly with ether to remove acetylacetone, and unaltered lithium sulphite was precipitated by adding absolute alcohol (1 vol.) to the aqueous layer. The filtrate was then concentrated under reduced pressure, a precipitate of red selenium was formed during evaporation, and the final mother-liquor, after being filtered through a layer of French chalk, was evaporated to dryness over sulphuric acid in a vacuum desiccator. This lithium salt separated in colourless, hexagonal plates, which rapidly deliquesced in air and decomposed subsequently with liberation of red selenium (Found: Se=25·55; Li=4·56. $Li_2S_2SeO_6,3H_2O$ requires Se=25·78; Li=4·56 per cent.).

Sodium selenodithionate tetrahydrate, $Se(SO_3Na)_2,4H_2O$, was prepared by adding 7 grams of selenium acetylacetone to 9 grams of sodium hydrogen sulphite in 30 c.c. of water. The liquid, which became appreciably hot, was cooled externally, and after thirty seconds the selenium acetylacetone had entirely disappeared, becoming replaced by a heavy, colourless, crystalline precipitate of the sodium salt. This product was dissolved in cold water and the filtered solution treated with alcohol, when the purified salt separated in colourless, prismatic needles (yield 80 per cent.) (Found: Se=21·80; Na=13·1; SO_2=17·7; H_2O=20·5. $Na_2S_2SeO_6,4H_2O$ requires Se=22·1; Na=12·9; SO_2=17·9; H_2O=20·2 per cent.). This hydrated salt, which was extremely soluble in cold water, very readily formed supersaturated solutions; it effloresced rapidly and passed into the anhydrous salt, $Se(SO_3Na)_2$, when exposed to a dry atmosphere.

Potassium selenodithionate (*loc. cit.*), the least soluble of the alkali selenodithionates, was obtained by neutralising a 2*N*-solution of selenodithionic acid and precipitating with alcohol.

Rubidium Selenodithionate, $Se(SO_3Rb)_2$.—Selenium acetylacetone (1·8 grams) was shaken mechanically for twenty minutes with 3·6 grams of rubidium hydrogen sulphite (page 1069) in 10 c.c. of water, when the rubidium salt separated in small, colourless needles. This product was dissolved in cold water and reprecipitated by alcohol (yield 76 per cent.) (Found: Se=19·3; Rb=41·8; SO_2=15·4. $Rb_2S_2SeO_6$ requires Se=19·3; Rb=41·7; SO_2=15·6 per cent.).

Rubidium selenodithionate, which was obtained in well-defined, colourless prisms, was more soluble in water than the potassium salt, but less so than the sodium and cæsium salts.

Cæsium selenodithionate, $Se(SO_3Cs)_2$, prepared by the interaction of selenium acetylacetone and cæsium hydrogen sulphite as in the preceding preparation, crystallised from hot, dilute alcohol in colourless, filamentous needles (yield 87 per cent.) and from water in transparent, tabular prisms [Found: Se=15·9; Cs=52·6; SO_2=12·4; SO_4 (from residue on heating)=19·0. $Cs_2S_2SeO_6$ requires Se=15·6; Cs=52·7; SO_2=12·7; SO_4=19·0 per cent.]. This cæsium salt has greater capacity for crystallising than any other alkali selenodithionate.

Ammonium selenodithionate, $Se(SO_3NH_4)_2$, prepared by double decomposition between selenium acetylacetone and ammonium hydrogen sulphite, was a somewhat unstable salt; it separated at first as a mass of colourless needles (yield 84 per cent.), which rapidly reddened on exposure to air (Found: Se=28·4; NH_4=12·7. $(NH_4)_2S_2SeO_6$ requires Se=28·8; NH_4=13·1 per cent.). On reprecipitating dissolved ammonium selenodithionate with alcohol-ether, colourless needles were obtained, which soon assumed a fawn colour.

Barium Selenodithionate, $Se(SO_3)_2Ba,2H_2O$.—Selenium acetylacetone (7 grams) was shaken mechanically with 9 grams of barium sulphite suspended in 26 c.c. of 3·3*N*-sulphurous acid. After seven hours, the organic compound was replaced by a heavy, colourless, crystalline precipitate of the barium salt. When redissolved in water and precipitated by alcohol, barium selenodithionate separated in colourless needles, which reddened on prolonged exposure (yield 70 per cent.) (Found: Se=19·1; Ba=33·1; SO_2=15·7; SO_4 (from residue) =23·2; H_2O=8·9. $BaS_2SeO_6,2H_2O$ requires Se=19·2; Ba=33·3; SO_2=15·5; SO_4=23·3; H_2O=8·7 per cent.).

Attempts to prepare the corresponding calcium salt showed that this compound was extremely soluble in water or alcohol and was not precipitated by ether from either of these solutions.

In the course of the foregoing preparations the following salts were characterised.

Rubidium hydrogen sulphite, $RbHSO_3$, obtained by passing sulphur dioxide into a solution of rubidium carbonate until a pale green tint was assumed, was precipitated by alcohol as a voluminous, white precipitate, which separated in colourless prisms (yield 80 per cent.). This salt, which was readily soluble in water, gave acid reactions with litmus and phenolphthalein, but was neutral to methyl-orange (Found: Rb=51·5; SO_3H=48·5. $RbHSO_3$ requires Rb=51·4; SO_3H=48·7 per cent.). When gradually heated to redness, dry rubidium hydrogen sulphite evolved water, sulphur, and sulphur dioxide, leaving a residue of rubidium sulphate.

Rubidium Sulphite.—(*a*) *Alcoholate.* A solution of rubidium carbonate was divided into two equal portions; one portion was treated with sulphur dioxide and the hydrogen sulphite precipitated by alcohol. The hydrogen sulphite was added to the other portion of rubidium carbonate solution, carbon dioxide was eliminated by heating, and a large excess of absolute alcohol added to the cooled solution. A heavy, oily, milky liquid was precipitated, which in a freezing mixture slowly set to a colourless, crystalline mass. The product was washed with a mixture of alcohol and ether and dried over calcium chloride (Found: Rb=62·0; $C_2H_5{\cdot}OH$=8·7. $2Rb_2SO_3,C_2H_5{\cdot}OH$ requires Rb=62·4; $C_2H_5{\cdot}OH$= 8·4 per cent.). The alcoholate readily gave up its alcohol on heating, and was freely soluble in water.

(*b*) *Anhydrous Salt.*—The alcoholate was dissolved in just sufficient water for solution, and evaporated by boiling under reduced pressure until a white, crystalline powder was deposited (Found: after drying on porous tile over sulphuric acid, Rb=68·3; SO_2=25·9. Rb_2SO_3 requires Rb=68·1; SO_2=25·5 per cent.).

Anhydrous *rubidium sulphite* consisted of small, colourless, prismatic tablets, extremely soluble in water and aqueous alcohol, reacted strongly alkaline to litmus, evolved sulphur dioxide with dilute mineral acids, and on ignition gave a residue of rubidium sulphate and sulphide.

Reactions of Selenodithionates.

Solutions of	Silver nitrate	Brownish-black precipitate.
	Mercurous nitrate	Greenish-black precipitate.
	Mercuric chloride	Yellow precipitate, becoming orange, then buff, and turning black on boiling.
	Stannous chloride	Becomes slowly milky, then pale yellow precipitate formed, becoming orange-yellow and turning orange-red on boiling.
	Hydrogen peroxide	Red selenium precipitated on boiling.
	Sodium hyposulphite	Red selenium precipitated in the cold.
	$KMnO_4+2N\text{-}H_2SO_4$	Decolorised, then turns yellow, then green, and bronze-green precipitate formed.
	Hydrogen sulphide	Yellow precipitate, turning orange-red on boiling.
	$2N$-HCl and $2N\text{-}HNO_3$	Red selenium separates on boiling.
	$4N\text{-}H_2SO_4$ or weaker	No reaction even on boiling.

The authors desire to express their thanks to the Department of Scientific and Industrial Research for grants which have partly defrayed the expense of this investigation.

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CXVII.—*Diazo-derivatives of 4′-Amino-1-phenyl-5-methylbenzothiazole (Dehydrothio-*p*-toluidine).*

By GILBERT T. MORGAN and DOROTHY WEBSTER.

THE stereochemical theory of diazo-compounds advocated by Hantzsch and accepted generally by workers in this field of organic chemistry is based on the existence in two isomeric forms of the aromatic diazo-cyanides, diazosulphonates, and diazo-oxides.

Of these two series, the more stable *anti*-diazo-compounds have frequently been prepared in a state of purity, so that their existence has been demonstrated by many analyses. The labile *syn*-diazo-compounds, on the other hand, are much less readily isolated, and analytical data in support of their existence as definite chemical entities are not always obtainable.

It should, however, be possible, by the selection of a base giving rise to exceptionally stable diazo-compounds, to obtain more decisive analytical evidence for or against the existence of the *syn*-diazo-series. 4′-Amino-1-phenyl-5-methylbenzothiazole (dehydrothio-*p*-toluidine) was shown by its discoverer to give rise to a diazo-chloride which is quite stable in solution at the ordinary temperature (A. G. Green, T., 1889, **55**, 227). It therefore seemed likely that this thiazole base would furnish other stable diazo-derivatives.*

When suspended in absolute alcohol and diazotised with ethyl nitrite, 4′-amino-1-phenyl-5-methylbenzothiazole hydrochloride yields two isomeric compounds, an insoluble diazo-chloride and a soluble one precipitated on the addition of ether. These products have properties resembling those of the *syn*- and *anti*-diazocyanides derived from simpler aromatic amines.

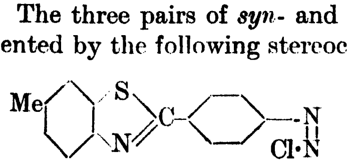
The soluble syn-1-*phenyl*-5-*methylbenzothiazole*-4′-*diazochloride*, which decomposes at a much lower temperature than its isomeride, dissolves readily in water, couples immediately with alkaline β-naphthol, and evolves nitrogen on treatment with copper bronze, giving rise to 4′-chloro-1-phenyl-5-methylbenzothiazole.

The anti-1-*phenyl*-5-*methylbenzothiazole*-4′-*diazochloride* is insoluble in water or alcohol, does not couple with alkaline β-naphthol, and reacts very slowly with copper bronze.

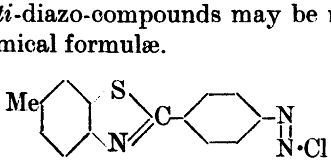
Ice-cold solutions of the *syn*-diazo-chloride, when treated with alkaline sodium sulphite, yield *sodium* syn-1-*phenyl*-5-*methylbenzothiazole*-4′-*diazosulphonate*, a compound coupling with β-naphthol, whereas at the ordinary temperature (about 20°) the isomeric, non-coupling *sodium* anti-1-*phenyl*-5-*methylbenzothiazole*-4′-*diazosulphonate* is obtained.

Similar experimental conditions lead to the formation of syn- and anti-1-*phenyl*-5-*methylbenzothiazole*-4′-*diazocyanides*.

The three pairs of *syn*- and *anti*-diazo-compounds may be represented by the following stereochemical formulæ.



(I.) (CN)
($NaSO_3$)



(II.) (CN)
(SO_3Na)

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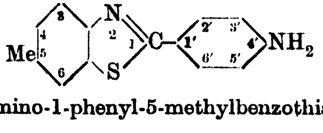
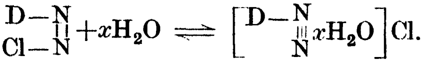
* The nomenclature and notation adopted in this communication are exemplified by the following numbered formula :



4′-Amino-1-phenyl-5-methylbenzothiazole.

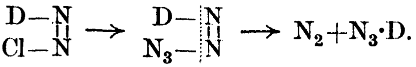
Qualitative evidence was also obtained of the existence of the *syn*- and *anti*-sodium diazo-oxides, but in this case the products were not isolated in a state of purity.

The solubility in water of the *syn*-diazo-chloride and -cyanide suggests that these compounds pass readily into the diazonium condition. If D is the aromatic complex, this equilibrium would be represented as follows :



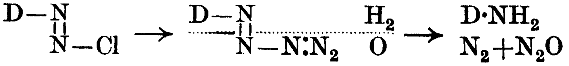
$$\begin{matrix} D-N \\ \| \\ Cl-N \end{matrix} + xH_2O \rightleftharpoons \left[\begin{matrix} D-N \\ \vert\vert\vert\, xH_2O \\ N \end{matrix} \right] Cl.$$

On adding sodium azide to the aqueous solution of the *syn*-diazo-chloride, nitrogen is evolved in the cold with the formation of *4′-triazo-1-phenyl-5-methylbenzothiazole* (III) :

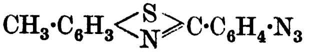


$$\begin{matrix} D-N \\ \| \\ Cl-N \end{matrix} \rightarrow \begin{matrix} D-\vdots N \\ \| \\ N_3-\vdots N \end{matrix} \rightarrow N_2+N_3\cdot D.$$

When the insoluble *anti*-diazo-chloride is warmed with aqueous sodium azide, 4′-amino-1-phenyl-5-methylbenzothiazole is regenerated, while nitrogen and nitrous oxide are evolved :

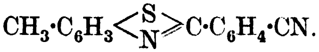


$$\begin{matrix} D-N \\ \| \\ N-Cl \end{matrix} \rightarrow \begin{matrix} D-N \cdots\cdots\cdots\cdots & H_2 \\ \| & \\ N-N{:}N_2 & O \end{matrix} \rightarrow \begin{matrix} D\cdot NH_2 \\ N_2+N_2O \end{matrix}$$



$CH_3\cdot C_6H_3{<}{}^{S}_{N}{>}C\cdot C_6H_4\cdot N_3$

(III.)



$CH_3\cdot C_6H_3{<}{}^{S}_{N}{>}C\cdot C_6H_4\cdot CN.$

(IV.)

4′-Amino-1-phenyl-5-methylbenzothiazole gives rise to a series of sparingly soluble, coloured diazo-salts, namely, the *diazo-nitrate, acid diazo-chromate, diazo-nitroprusside, diazo-ferrocyanide, acid diazo-carbonate, diazo-orthoborate* and *diazo-chlorate.*

With the exception of the last substance, which is extremely explosive at the ordinary temperature, the members of this series are stable in the solid condition at the ordinary temperature; they all couple readily with alkaline β-naphthol. These properties are consistent with the view that the foregoing diazo-derivatives belong to the *syn*-series.

EXPERIMENTAL.

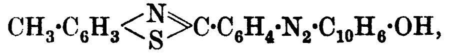
4′-Amino-1-phenyl-5-methylbenzothiazole (dehydrothio-*p*-toluidine) was prepared by heating together at 180° for eight hours 100 grams of *p*-toluidine and 60 grams of sulphur, the fusion being heated subsequently at 250° for twenty hours. The product was worked up by Green's method (*loc. cit.*); the monothiazole base, after repeated crystallisation from amyl alcohol, melted at 191°.

syn- *and* anti-1-*Phenyl-5-methylbenzothiazole-4′-diazochlorides* (Formulæ I and II).

4′-Amino-1-phenyl-5-methylbenzothiazole (15 grams) was converted into the hydrochloride by treatment with excess of alcoholic hydrochloric acid. The dry hydrochloride was suspended in about 50 c.c. of absolute alcohol and treated at 0° with 9 grams of ethyl nitrite in 50 c.c. of the same solvent. The sparingly soluble *anti*-diazo-chloride (2 grams) which separated was extracted successively with boiling chloroform, cold water, and again with chloroform, the extraction with the organic solvent being repeated fourteen times (Found: C=57·36; H=3·57; N=14·41; Cl=12·67; S=11·02. $C_{14}H_{10}N_3ClS$ requires C=58·51; H=3·50; N=14·58; Cl=12·30; S=11·12 per cent.). This *anti*-diazo-compound, a brownish-yellow, amorphous powder, melted with decomposition at 270°; it was insoluble in water and did not couple with alkaline β-naphthol until after treatment with hydrochloric acid.

The soluble *syn*-diazo-chloride (9·5 grams), which was precipitated from the foregoing alcoholic solution by adding excess of ether, melted with decomposition at 139° (Found: C=56·94; H=3·88; N=14·31; Cl=12·13; S=10·75 per cent.).* The *syn*-diazo-compound was very soluble in water and coupled readily with alkaline β-naphthol to a red azo-pigment, becoming violet with concentrated sulphuric acid.

1-*Phenyl-5-methylbenzothiazole-4′-azo-β-naphthol*,



$$CH_3{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{N}{S}{>}C{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH,$$

crystallised from glacial acetic acid in intensely crimson needles melting at 214° and assuming a violet colour in concentrated sulphuric acid (Found: N=10·65; S=8·23. $C_{24}H_{17}ON_3S$ requires N=10·60; S=8·09 per cent.).

A repetition of the diazotisation with amyl nitrite, using ethyl alcohol, led to a smaller yield of the *syn*-diazo-compound contaminated with a viscid by-product. In dilute hydrochloric acid, diazotisation led to the production of the soluble *syn*-diazo-compound, but, on boiling, the solution lost its intense coupling power and yielded a reddish-brown solid melting at 255°, identified as 4′-hydroxy-1-phenyl-5-methylbenzothiazole (Jacobson, *Ber.*, 1889, **22**, 334) (Found: N=5·66. Calc., N=5·79 per cent.). The aqueous solution of the *syn*-diazo-chloride, when treated in the cold with copper bronze, evolved nitrogen forthwith and in two hours the coupling power had disappeared. The chloro-derivative, when crystallised repeatedly from acetone, separated in pale yellow, granular nodules melting at 160° (Found: N=5·52; Cl=13·47; S=11·98. $C_{14}H_{10}NClS$ requires N=5·38; Cl=13·62; S=12·32 per cent.).

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* In the analyses of the isomeric diazo-chlorides, the carbon estimation, repeated several times, was consistently low, although the other constituents gave numbers agreeing very closely with the calculated values.

4′-Chloro-1-phenyl-5-methylbenzothiazole was insoluble in water and dissolved readily in the volatile organic media excepting ethyl alcohol, in which it was only sparingly soluble.

The *anti*-diazo-chloride (2 grams), when treated with copper bronze in dilute hydrochloric acid, remained unchanged for several hours, but after a week had yielded the above chloro-compound (m. p. 160°).

Potassium syn- *and* anti-1-*Phenyl-5-methylbenzothiazole-4′-diazo-oxides.*

A 15 per cent. solution of *syn*-1-phenyl-5-methylbenzothiazole-4′-diazo-chloride (2 grams) was added to 90 grams of potassium hydroxide in 60 c.c. of water at 5°, when a pink precipitate separated. This product, which was very soluble in cold water, coupled immediately with alkaline β-naphthol; it was not, however, obtained in a sufficiently pure state for analysis.

The foregoing alkaline solution was heated at 110° until the coupling power was lost. The *syn*-compound dissolved partly; the final residue of the *anti*-diazo-oxide, which was of a darker colour, no longer interacted with alkaline β-naphthol until it had first been acidified.

Action of Sodium Azide on the syn- *and* anti-1-*Phenyl-5-methylbenzothiazole-4′-diazo-chlorides.*

A slight excess of sodium azide was added to a cooled aqueous solution of the purified *syn*-diazo-chloride, nitrogen was evolved, and a pale pink precipitate of *4′-triazo-1-phenyl-5-methylbenzothiazole* (III) was produced, which changed to a light brown on drying; it melted at 121° (Found: N=21·74. $C_{14}H_{10}N_4S$ requires N=21·00 per cent.).

A slight excess of sodium azide was gently warmed for half an hour with an aqueous suspension of the purified *anti*-diazo-chloride. The product melted at 182—184° and after purification was identified as the original amine by its melting point (186°) by analysis (Found: N=11·44. Calc., N=11·63 per cent.), and by the formation of the acid diazo-chromate and the azo-β-naphthol.

The reactions with sodium azide were conducted in a gas-apparatus. The *syn*-diazo-chloride evolved nitrogen (Found:

$N=9{\cdot}33$, $9{\cdot}24$). The *anti*-diazo-chloride evolved about twice as much gas, the amount varying with the age of the preparation (Found: $N_2O=16{\cdot}24$, $14{\cdot}96$; $N=10{\cdot}68$, $9{\cdot}54$. Calc., $N_2O=15{\cdot}27$; $N=9{\cdot}72$ per cent.).

Sodium syn- *and* anti-1-*Phenyl-5-methylbenzothiazole-4′-diazosulphonates* (Formulæ I and II).

An aqueous solution of the *syn*-diazo-chloride, prepared in the foregoing manner, was added slowly to a solution of sodium sulphite and sodium hydroxide cooled to 0°. After twenty minutes, the alkaline solution was filtered from an orange-brown, amorphous precipitate. This product, after five extractions with chloroform, melted with decomposition at 202° (Found: $N=11{\cdot}66$; $S=18{\cdot}07$; $Na=6{\cdot}41$. $C_{14}H_{10}O_3N_3S_2Na$ requires $N=11{\cdot}81$; $S=18{\cdot}01$; $Na=6{\cdot}46$ per cent.). This syn-*diazosulphonate* coupled readily with alkaline β-naphthol, yielding the foregoing azo-derivative.

The *anti*-diazosulphonate was obtained as in the foregoing preparation excepting that the alkaline sulphite solution was maintained at the ordinary temperature. The orange precipitate assumed almost instantly a brown colour and after four extractions with chloroform a yellow, amorphous product was left, melting with decomposition at 309° (Found: $N=11{\cdot}08$; $S=17{\cdot}12$; $Na=6{\cdot}54$ per cent.). This *anti*-compound did not couple with alkaline β-naphthol unless it had first been treated with hydrochloric acid.

syn- *and* anti-1-*Phenyl-5-methylbenzothiazole-4′-diazo-cyanides* (Formulæ I and II).

The syn-*diazo-cyanide* was formed on adding 2 grams of potassium cyanide and 5 c.c. of water to 2 grams of the *syn*-diazo-chloride dissolved in 30 c.c. of water acidified with hydrochloric acid, and cooled below 0°. The bright brick-red product, which was very soluble in water, decomposed at 131°, coupled readily with alkaline β-naphthol, and quickly lost nitrogen with copper bronze (Found: $N=19{\cdot}44$; $S=11{\cdot}62$. $C_{15}H_{10}N_4S$ requires $N=20{\cdot}09$; $S=11{\cdot}49$ per cent.).

The anti-*diazo-cyanide*, obtained by adding 0·5 gram of potassium cyanide to 2 grams of the *syn*-diazo-chloride in 15 c.c. of water at 5°, separated as a deep orange precipitate insoluble in water; after crystallisation from moist acetone, it melted at 175°, and did not couple directly with alkaline β-naphthol. With copper bronze it evolved nitrogen, but much more slowly than in the case of the *syn*-compound (Found: $N=20{\cdot}40$; $S=11{\cdot}98$. $C_{15}H_{10}N_4S$ requires $N=20{\cdot}09$; $S=11{\cdot}49$ per cent.).

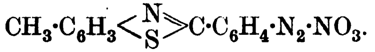
4'-Cyano-1-phenyl-5-methylbenzothiazole (Formula IV).

On adding copper bronze to an acid solution of the *syn*-diazocyanide, nitrogen was evolved immediately and a yellow solid separated, which on repeated crystallisation from acetone melted at 145° (Found: N=11·19; S=13·10. $C_{15}H_{10}N_2S$ requires N=11·17; S=12·78 per cent.). This cyano-derivative was rather yellower than the corresponding chloro-compound and had a similar solubility in the usual organic media.

syn-*1-Phenyl-5-methylbenzothiazole-4'-diazo-salts.*

The following sparingly soluble diazo-salts coupled readily with alkaline β-naphthol and belonged evidently to the *syn*-series.

1-Phenyl-5-methylbenzothiazole-4'-diazonitrate,



$$\mathrm{CH_3{\cdot}C_6H_3}<\!\genfrac{}{}{0pt}{}{\mathrm{N}}{\mathrm{S}}\!>\mathrm{C{\cdot}C_6H_4{\cdot}N_2{\cdot}NO_3}.$$

—Sodium nitrite was added to a solution of the aminothiazole (2 grams) in 20 c.c. of concentrated nitric acid, keeping the temperature at 0°. A yellowish-brown precipitate (1·5 grams) separated on adding water, which, when dry, exploded at 145° (Found: N=18·11; S=10·31. $C_{14}H_{10}O_3N_4S$ requires N=17·80; S=10·18 per cent.).

The *acid diazo-chromate,* $(C_{14}H_{10}NS{\cdot}N_2)HCrO_4$, obtained as a copious yellow precipitate on adding excess of potassium dichromate to an aqueous solution of the *syn*-diazo-salt, detonated at 120° (Found: N=11·44; Cr=14·25. $C_{14}H_{11}O_4N_3SCr$ requires N=11·36; Cr=14·10 per cent.).

The *diazo-nitroprusside,* $(C_{14}H_{10}NS{\cdot}N_2)_2FeNO(CN)_5$, prepared from the diazo-chloride by double decomposition with sodium nitroprusside, was a bright yellow, amorphous powder exploding at 140° (Found: N=22·48; Fe=7·90. $C_{33}H_{20}ON_{12}S_2Fe$ requires N=23·29; Fe=7·74 per cent.).

The *diazo-ferricyanide,* $(C_{14}H_{10}NS{\cdot}N_2)_3Fe(CN)_6$, was a greenish-yellow powder melting at 158° (Found: N=22·13; Fe=5·85. $C_{48}H_{30}N_{15}S_3Fe$ requires N=21·65; Fe=5·75 per cent.).

The *acid diazo-carbonate,* $(C_{14}H_{10}NS{\cdot}N_2)HCO_3$, prepared by double decomposition from the *syn*-diazo-chloride and sodium hydrogen carbonate, was a reddish-brown, amorphous powder melting at 128° with slight detonation; it effervesced with dilute sulphuric acid (Found: N=13·56; S=10·24. $C_{15}H_{11}O_3N_3S$ requires N=13·39; S=10·21 per cent.).

The *diazo-chlorate,* $(C_{14}H_{10}NS{\cdot}N_2)ClO_3$, a brilliant yellow, amorphous compound obtained by double decomposition, was slightly soluble in water. When dried, it was found to be extremely explosive, detonating violently at 110° (Found: N=12·59. $C_{14}H_{10}O_3N_3ClS$ requires N=12·50 per cent.).

The *diazo-orthoborate*, $(C_{14}H_{10}NS\cdot N_2)_3BO_3$, was obtained as a bright brown powder by adding excess of concentrated borax solution (1 gram in 30 c.c.) to a solution of the *syn*-diazo-chloride; it melted at 154° with decomposition (Found: N=15·47; S=11·51. $C_{42}H_{30}O_3N_9S_3B$ requires N=15·42; S=11·76 per cent.). This orthoborate was soluble in chloroform and was precipitated therefrom by light petroleum.

The authors' thanks are due to the Advisory Council of the Department of Scientific and Industrial Research for a grant which has partly defrayed the expenses of this investigation.

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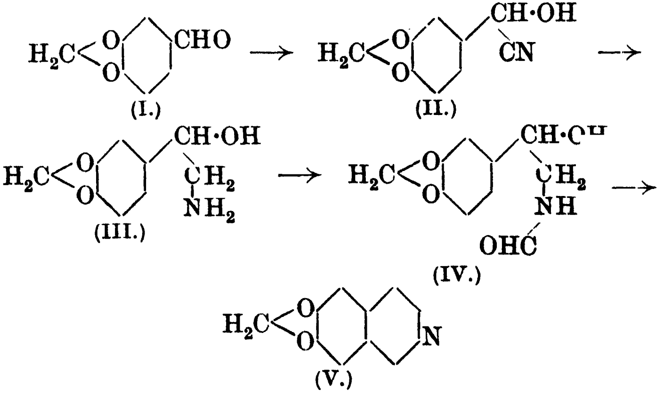
CXVIII.—*β-Hydroxy-β-3 : 4-methylenedioxyphenylethylamine and its Derivatives.*

By FREDERICK ALFRED MASON.

SUBSTANCES of the type $R\cdot CH(OH)\cdot CH_2\cdot NH_2$ are of considerable interest owing to their relationships on the one hand to adrenaline, $C_6H_3(OH)_2\cdot CH(OH)\cdot CH_2\cdot NHMe$, and similar sympathomimetic products, and on the other to derivatives of *iso*quinoline.

The present investigation was begun with the hope of effecting a convenient synthesis of 6 : 7-methylenedioxy*iso*quinoline (V) from piperonaldehyde (I) by the steps shown:



The formyl derivative (IV) was obtained, but as the investigation had to be abandoned at this stage it has seemed desirable to place on record the results obtained.*

Various investigators have prepared adrenaline methylene ether from β-bromo-α-3 : 4-methylenedioxyphenylethyl alcohol (Barger and Jowett, T., 1905, **87**, 967; Barger, T., 1908, **93**, 2081; Pauly and Neukam, *Ber.*, 1908, **41**, 4151; Böttcher, *Ber.*, 1909, **42**, 253; Mannich, *Arch. Pharm.*, 1910, **248**, 127; D.R.-P. 209609, 209610, 212206), but the corresponding unmethylated compound (III) does not appear to have been prepared hitherto.†

The method adopted for the preparation of β-hydroxy-β-3 : 4-methylenedioxyphenylethylamine (III) was substantially that described by the Farbwerke Hoechst (D.R.-P. 193634; Eng. Pat. 27117, 1907) and consisted in the reduction of piperonaldehyde-cyanohydrin (II) in alcoholic solution by means of sodium amalgam. The method was extremely laborious and difficult to control, yields being obtained which varied from nothing up to about 17 per cent., although the latter yield was only obtained on very few occasions.

Other methods of reduction were also tried, for example, magnesium and acetic acid, magnesium amalgam, and aluminium amalgam, but no trace of the base was obtained.

Attempts to reduce the cyanohydrin electrolytically in a 50 per cent. alcoholic solution of potassium acetate with an ice-cooled potassium amalgam cathode and a water-cooled platinum anode were unsuccessful, as also were similar attempts with a sodium amalgam electrode and an aqueous-alcoholic solution of sodium acetate.

Preliminary experiments with the small amount of the formyl derivative available failed to give any detectable amount of 6 : 7-methylenedioxy*iso*quinoline by the interaction of the formyl compound and phosphoric oxide in toluene, but there can be little doubt that further work with a larger quantity of the substance would lead to the desired product, by Pictet and Gams's method for the synthesis of *iso*quinoline itself (*Ber.*, 1910, **43**, 2384).

EXPERIMENTAL.

β-*Hydroxy*-β-3 : 4-*methylenedioxyphenylethylamine* (Formula III).

The pasty mass obtained by adding sodium hydrogen sulphite (120 grams) dissolved in water (120 c.c.) to a solution of piperonaldehyde (50 grams) in warm alcohol (50 c.c.) was treated with potassium cyanide (50 grams) dissolved in water (200 c.c.) and the mixture stirred and gently shaken, care being taken to avoid emulsification, until the solid had almost disappeared. After the mixture had been kept for a few minutes the lower layer of the cyanohydrin thus obtained was run into a mixture of 600 c.c. of 95 per cent. alcohol and 400 c.c. of water cooled in a freezing mixture, and to the well-stirred solution were added 2500 grams of 4 per cent. sodium amalgam, in portions of 250 grams at intervals of about fifteen minutes, 250 c.c. of glacial acetic acid being run in at a suitable rate to keep the liquid faintly acid to phenolphthalein; the temperature was maintained at 6—8°. After about three hours the alcoholic layer was filtered from the large amount of sodium acetate formed, and from a small amount of tarry greenish-yellow by-product, which was not further examined, and the clear yellow filtrate was evaporated under 40 mm. pressure until all the alcohol had been removed. The aqueous layer, after being shaken thrice with ether * to remove the yellow oil that had separated, was made strongly alkaline with sodium hydroxide solution and extracted six times with an equal volume of ether, or better with a smaller quantity of chloroform, care being taken that the solvent did not become emulsified by too vigorous shaking. The extracts were dried with potassium carbonate, and the solvent was evaporated. The residue, consisting of a few c.c. of a thin yellow oil, easily soluble in alcohol or chloroform, insoluble in water, and sparingly soluble in ether, was covered with 30 c.c. of ether and concentrated hydrochloric acid added drop by drop with stirring until no further salt formation was observed. The oil solidified quickly to a white, crystalline paste of crude β-hydroxy-β-3 : 4-methylenedioxyphenylethylamine hydrochloride, which was filtered and pressed on porous tile; the yield was 12 grams or 17 per cent. of the theoretical.

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* The investigation was carried out at various times during the period June 1914 to December 1915, when it was abandoned owing to the pressure of war work.

† For further details of related compounds, see G. Barger, "Simpler Natural Bases" (London 1914), pp. 81—105; and Meyer and Jacobson, "Organische Chemie," 2, III, (3) pp. 1014 *et seq.*, which gives full references to the literature.

Derivatives of the Base.

The *hydrochloride* was easily soluble in water and in alcohol, from which it separated in white, prismatic crystals, m. p. 176° (Found: C=49·5; H=5·8; Cl=16·6. $C_9H_{12}O_3NCl$ requires C=49·6; H=5·5; Cl=16·3 per cent.).

The *formate*, obtained in a similar manner by the addition of formic acid to the ether or chloroform solution of the base, formed white crystals, m. p. 138—139°, which were easily soluble in water and alcohol (Found *: C=53·4. $C_{10}H_{13}O_5N$ requires C=52·9 per cent.).

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* The ethereal extracts, after removal of the solvent, left a large amount of oily product, which, on keeping, deposited large, yellow crystals of low melting point. The substance was extremely soluble in alcohol and consisted probably of piperonyl alcohol, but was not further examined.

The *platinichloride*, obtained in the usual manner from the hydrochloride, formed brilliant orange scales, which were moderately soluble in water or alcohol, and blackened and decomposed above 170—200°.

The *urethane* derivative, $CH_2{:}O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CH_2{\cdot}NH{\cdot}CO_2Et$, was prepared by treating a solution of the hydrochloride with ethyl chloroformate and excess of sodium carbonate solution, when it was deposited in minute, colourless crystals, m. p. 105°, insoluble in water, and easily soluble in chloroform or alcohol.

The *benzoyl* derivative, $C_9H_9O_3{\cdot}NH{\cdot}COPh$, was prepared by treating a solution of the hydrochloride with an ethereal solution of benzoyl chloride in presence of a little sodium carbonate solution. After recrystallisation from 50 per cent. alcohol, it formed glistening, white leaflets, m. p. 155—157°, easily soluble in alcohol, sparingly soluble in ether, and insoluble in water.

The *mono*-p-*nitrobenzoyl* derivative, $C_9H_9O_3{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$, was obtained by shaking 11·7 grams of the formate dissolved in 25 c.c. of water and a solution of 28·6 grams of sodium carbonate with 10 grams of *p*-nitrobenzoyl chloride dissolved in 25 c.c. of chloroform. The thick, crystalline, yellow precipitate was recrystallised from alcohol and the p-*nitrobenzoyl* derivative thereby obtained in small, yellow leaflets, m. p. 155—157°, soluble in alcohol, sparingly soluble in chloroform, and insoluble in water (Found: C=58·3; H=4·7. $C_{16}H_{14}O_6N_2$ requires C=58·2; H=4·22 per cent.).

The *di*-p-*nitrobenzoyl* derivative,

$$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_9H_8O_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2,$$

was obtained when solutions of 6 grams of the mono-acyl derivative, 6 grams of *p*-nitrobenzoyl chloride, and 3·5 c.c. of pyridine, each dissolved in 10 c.c. of chloroform, were mixed and boiled for one hour. The solvent was then evaporated and the residue triturated first with a few c.c. of alcohol until it set to a crystalline mass, then with a little sodium carbonate solution. After being filtered, washed with a few c.c. of alcohol, dried, and recrystallised from chloroform, the *di*-p-*nitrobenzoyl* derivative was obtained in small, orange-yellow crystals, m. p. 179—180°, which were sparingly soluble in most solvents.

The *veratroyl* derivative, $C_9H_9O_3{\cdot}NH{\cdot}CO{\cdot}C_6H_3(OMe)_2$, was prepared from 4·5 grams of the formate dissolved in 5 c.c. of water and 4 grams of veratroyl chloride in 10 c.c. of dry ether, sodium carbonate being added until the alkalinity was permanent. The extract in chloroform of the yellow oil that separated was dried over potassium carbonate and the solvent evaporated, when a viscous, uncrystallisable gum was obtained, which, on evaporation in a vacuum, frothed up to a friable, resinous mass melting indefinitely at 60—80°. It was insoluble in water, ether, benzene, or light petroleum, but was very easily soluble in methyl or ethyl alcohol and in chloroform.

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* The analysis was kindly carried out by Dr. P. W. Robertson by his method (T., 1916, **109**, 215).

The *formyl* derivative, $C_9H_9O_3{\cdot}NH{\cdot}CHO$, could be prepared satisfactorily neither by heating the base or its hydrochloride with formic acid, nor by heating the formate at 110°. It was obtained by boiling the base with purified formic ester and after recrystallisation from methyl alcohol formed hard, white crystals melting at 90—92°. It was insoluble in water, carbon disulphide, or ether, very sparingly soluble in hot benzene, easily soluble in hot methyl alcohol, but only slightly soluble in the cold solvent; it dissolved readily in ethyl alcohol, chloroform, or formic ester.

The author wishes to express his thanks to Prof. H. B. Baker for his kind interest and encouragement during the work, which was carried out in the Chemistry Department of the Royal College of Science, South Kensington, and also to the Chemical Society for a grant which defrayed part of the expenses incurred.

[*Received, March* 19*th*, 1921.]

CXIX.—*Overvoltage. Part I. A Comparison of the Methods of Determination, especially as Applied to the Mercury Cathode.*

By SYDNEY DUNNILL.

THERE are two main difficulties which stand in the way of a quantitative theory of overvoltage.

(1) Metallic surfaces cannot be reproduced exactly, and their properties change during the passage of the current.

(2) There is still a considerable difference of opinion as to which of the methods of determination gives the true value, namely, the "commutator method," by which the potential of the electrode is measured at a small interval, say 0·012 second, after the main

current has been cut off, or the "direct method," by which the potential is taken while the current is flowing. The first difficulty, however, does not arise in the case of the mercury cathode, and hence that was the electrode with which the present investigation was begun.

The most complete studies of the mercury cathode are those of Tafel (*Zeitsch. physikal. Chem.*, 1905, **50**, 641), Lewis and Jackson (*ibid.*, 1906, **56**, 193), and Newbery (T., 1914, **105**, 2419; 1916, **109**, 1051).

Tafel employed the direct method upon a mercury surface of 25 sq. cm. The results from overvoltages of 1·0 volt to 1·2 volts could be represented by the equation $E=a+b \log I$, where E is the overvoltage, I is the current, and a and b are constants. Lewis and Jackson, also using the direct method, measured the overvoltage at a mercury cathode contained in a tube of 0·2 cm. diameter. The same form of equation was found to hold from overvoltages of 0·3 volt, but at about 0·7 volt the readings became unsteady and the measurements were not carried further. At this point also, bubbles began to appear down the side of the tube to a distance of 1 cm. below the mercury surface. Newbery, using the commutator method, with the mercury in a tube of 1 sq. cm. cross-section, found exceedingly erratic overvoltages with a general tendency to decrease as the current was increased. At the highest current densities, zero and even negative readings were recorded.

The difference between the results given by the two methods is strikingly shown in the following table of overvoltages at a mercury cathode in N-sulphuric acid. The current density is given in milliamperes per square centimetre.

Current density.	Tafel.	Newbery.
1	1·07	—
10	1·18	0·54
40	1·24	—
100	—	0·30
1000	—	−0·01
2000	—	−0·05

EXPERIMENTAL.

With the object of using a definite volume of mercury, the first experiments were made with the mercury in a small cup blown on the end of a capillary tube. Progress, however, was found to be impossible, since the current could not be passed for more than a few minutes without the breaking of the mercury thread in the capillary owing to the formation of a bubble of gas.

Experiments were then made in which the mercury covered the bottom of a crystallising dish and at the edge was connected with the source of current by a platinum wire sealed into glass. The anode was a platinum wire suspended in the centre of the dish about 0·5 cm. above the mercury. *N*-Sulphuric acid was the first electrolyte used, in a dish of 11 cm. diameter.

Bubbles form quite smoothly over the surface until the current exceeds about 50 milliamperes. There now appears below the anode a circular patch quite free from bubbles. The diameter of the patch increases with increasing current and at 100 milliamperes is about 7 cm. By the observation of motes it can be seen that the mercury surface is flowing rapidly outwards from the centre. Thus the mercury, after receiving current, travels outwards for some distance before visible bubbles have time to form, the hydrogen being either in the mercury or in the solution near the surface. About 0·5 cm. within the circumference of the bare space there is a slight discontinuity, similar in appearance to the bevel on a mirror. Possibly this marks the limit of the actual movement of the mercury while the stream of solution clears away the bubbles for a short distance further.

The phenomenon is readily accounted for by a consideration of the electrocapillary curve. In *N*-sulphuric acid the potential of mercury at which hydrogen is being liberated is higher than the potential of mercury of maximum surface tension. Hence, the mercury in the centre, which is receiving most current, being at a higher potential, has a lower surface tension than that nearer the circumference, and because of this the mercury at the centre is being continuously dragged outwards. This view is confirmed by the following observations :

(1) The same phenomenon occurs, but more readily, when the mercury is acting as anode, that is, on the other branch of the curve. This can best be seen by removing the platinum connexion from the mercury and suspending it in the solution a short distance above the surface. The discontinuity is seen in this case also.

(2) With the mercury as cathode in mercurous nitrate solution, the surface tends to draw towards the centre. Here the potential is on the same branch of the curve as in (1), but the mercury is being polarised in the opposite sense, so that the mercury at the centre now has the higher surface tension.

(3) In alkaline solution, where the surface tension decreases rapidly with increasing cathodic polarisation, the ring is especially large. A normal solution of ammonium hydroxide containing in addition 66 grams of ammonium sulphate per litre was used as electrolyte in a 14 cm. dish arranged as before. With a current

of 100 milliamperes no gas appeared for several minutes and the whole surface of the mercury seemed to be travelling out to the edge. The flow continued underneath the mercury and small bubbles, together with some of the solution, were seen between the mercury and the bottom of the dish, moving towards the centre, where, no doubt, the ammonium amalgam was accumulating. The solution and the gas bubbles would collect together in places and occasionally burst through the mercury, leaving an effervescing patch which immediately floated on the mercury to the side of the dish. Apart from this, the surface remained quite blank. On opening the circuit the surface moved in a direction opposite to that previously observed and large areas of effervescing amalgam were drawn round the edges on to the upper surface of the mercury. In this case, in addition to the purely electrical effect, there will, of course, be some change of surface tension due to formation of the amalgam, although whether this produces an increase or a decrease is unknown.

Potential measurements were now made in order to determine the effect of this phenomenon on the overvoltage as given by the commutator method, since the motion of the mercury would be likely to cause a very rapid fall of potential when the current ceased to flow. The general arrangement of the apparatus was similar to that described by Newbery (T., 1914, **105**, 2419). The rotating commutator used was of the type known as the MacGregor drum. It was driven by an electric motor which could be set at three speeds, giving approximately 0·020 sec., 0·013 sec., and 0·010 sec. respectively as the mean interval between the interruption of the main current and the reading of the potential. When the commutator was applied, the mercury was thrown into stationary vibrations, which removed the bubbles from the surface except at the nodes, which were several millimetres apart. At higher speeds the distance between the nodes became less.

The mercury cathode filled a small, shallow, glass dish, connexion being made by a platinum wire sealed into a glass tube. The surface area of the mercury was approximately 10 sq. cm. The anode was of platinum foil contained in part of a test-tube drawn out to a point, leaving an opening of 0·1 cm. diameter. This was supported a few millimetres above the surface of the mercury.

The electrolyte was *N*-sulphuric acid and the potential was measured with reference to a mercurous sulphate electrode in the same solution. A capillary electrometer was used as zero instrument. The syphon connecting the main solution with the reference electrode terminated in a capillary of about 0·01 cm. internal diameter, which could be adjusted exactly to any point on the mercury surface. Except where otherwise stated, the capillary touched the mercury immediately below the anode.

All the experiments were made at room temperature, that is, at about 12°.

In the following table a few of the results are shown. The current is given in milliamperes. The figures are the overvoltages measured directly and with the three speeds of the commutator, assuming the combination $H_2 \mid N\text{–}H_2SO_4,Hg_2SO_4 \mid Hg$ to have an *E.M.F.* of 0·70 volt.

	Overvoltage.			
Current.	Direct.	0·010 sec.	0·013 sec.	0·020 sec.
36	1·14	0·85	0·82	0·75
68	1·23	0·83	0·79	0·71
68	1·22	0·73	0·67	0·51

The last series gives the results obtained when the solution was stirred by means of a stirrer with vanes driven at 250 revolutions per minute. It is seen that stirring had very little influence on the potential while the current was passing, as would be expected, since the mercury surface was already in rapid motion. The rate of decay, however, was considerably increased.

The overvoltage values obtained by the direct method were quite steady and after an initial rise were fairly accurately reproducible, a slight increase with time being most likely due to concentration changes. The following figures were obtained by means of the same apparatus as before, with the opening into the anode compartment 0·25 cm. above the centre of the cathode. The solution was stirred for a short time after each change in the applied *E.M.F.*, but was allowed to come to rest before the reading was taken.

On first passing a current of 11 milliamperes the centre of the cathode had an overvoltage of 0·85 volt, which became 0·87 volt at 22 milliamperes. Up till then no ring had appeared, but when the current was interrupted for a few seconds and applied again, a ring was formed, which still remained when the current was reduced to 11 milliamperes. Readings were then taken, the current being gradually increased to 78 and then brought back to lower values.

	Overvoltage.	
Current.	increasing.	decreasing.
11	0·93	0·94
20	1·02	1·02
35	1·11	1·12
50	1·18	
78	1·26	

The bare space becomes larger with increasing current, but the circumference does not remain at a constant potential. At 20 milliamperes, the diameter was about 1·8 cm. and the overvoltage at the boundary of the space was 1·00 volt, whilst at 78 milliamperes, with a ring of about 2·5 cm. diameter, the overvoltage at the circumference was 1·12 volts.

The overvoltages given above are similar to those of Tafel, although in his experiments a ring was most likely not formed owing to the more equal distribution of the current.

Since the mobility of the mercury surface introduces complications, experiments were made with a cathode of amalgamated lead. This consisted of a small rod of lead fixed into a glass tube with sealing wax and covered with paraffin wax except over an area of about 1 sq. cm. at the end, which was amalgamated. Mercury contained in a crystallising dish formed the anode. The electrolyte was *N*-hydrochloric acid. The potential was measured against a calomel electrode, also in *N*-hydrochloric acid, and connected as before with a fine capillary touching the cathode.

The solution was contained in a wide-mouthed bottle provided with a cork, through which passed the connexions and the sleeve of the stirrer. Hydrogen was bubbled through the solution for two days before readings were taken. The results were similar to those obtained for mercury, as is shown by the following example. The combination $H_2 \mid N\text{-}HCl,Hg_2Cl_2 \mid Hg$ is taken as having an *E.M.F.* of 0·28 volt.

	Overvoltage.			
Current.	Direct.	0·010 sec.	0·013 sec.	0·020 sec.
5	1·20	0·91	0·89	0·86
5	1·19	0·77	0·74	0·62

In the second series the solution was stirred.

Obviously the overvoltage decays too rapidly for any decision to be made as to the true value.

The same apparatus was used in the next experiments, except that the electrolyte was *N*-sodium hydroxide, with a reference electrode of mercuric oxide. A current of 1·2 milliamperes was maintained throughout the whole series. The overvoltage diminished while the current was passing to the extent of 0·2 volt in forty-five minutes and the cathode became dull owing to deposition of sodium. The following is a typical set of consecutive readings

$$(H_2 \mid N\text{–}NaOH,HgO \mid Hg = -0{\cdot}930 \text{ volt}).$$

Direct.		0·020 sec.	0·013 sec.	0·010 sec.	Direct.
0·875	0·878	0·852	0·855	0·856	0·870

It seems scarcely justifiable to compare the results when a direct current is used with those obtained by means of the intermittent current. The second drum of the commutator enabled the potential to be taken during the latter half of the period in which the current was passing, leaving the electrometer circuit open during the remainder of the time. This potential is given in the second column above.

Discussion of Results.

The earlier experiments with the mercury cathode provide an explanation of several previous observations. A mercury cathode in a narrow tube where the sides are wet with the solution but are receiving very little current is in a similar condition to that of a pool of mercury with the current concentrated at one point on the surface. The outward flow of the mercury, bringing with it a layer of solution supersaturated with hydrogen and perhaps itself containing hydrogen in some form, is quite sufficient to account for the appearance of bubbles down the side of the tube. As the current is increased, the movement will become more rapid and the potential will fall more quickly should the current be interrupted. This is shown by the decreasing values obtained by the commutator method. The fall of potential is so rapid that small changes in the motion of the mercury, by changing the rate of decay, would produce erratic variations in the potential readings at a given interval of time.

The stationary waves produced by the commutator are in themselves sufficient to show that changes of surface tension, denoting changes of potential, take place during the interval in which no current is flowing.

Results previously obtained by the direct method have shown for all metals an increase of hydrogen overvoltage with the current, whereas the commutator method shows an increase in alkaline solution, but in acid solution there appears to be always a slight decrease. This is most likely owing to the stirring of the solution round the cathode by the bubbles of hydrogen, since, as is shown above, stirring considerably increases the rate of decay of the polarisation. At higher current densities more hydrogen is evolved and hence the stirring is more vigorous.

According to Newbery, the results obtained by the direct method are inaccurate owing to the electrical resistance of a film of gas which is said to be present on the electrode. It would be difficult to give a direct proof of the presence of this film. The paper by Newbery on "The Electrical Resistance of an Electrolytic Cell" (*Trans. Faraday Soc.*, 1919, **15**, Part I) contributes nothing to this discussion, since it is assumed at the outset that the difference between the overvoltages determined by the two methods is due to "transfer resistance," whereas a rapid fall of potential during the first one-hundredth of a second would have exactly the same effect. The "transfer resistance" was found to be very high at low current densities, but became much smaller when the current density was increased. This is owing to the fact that the fall of potential varies much less rapidly than the current, so that at higher current densities the hypothetical resistance necessary to account for the loss of *E.M.F.* becomes smaller.

However, the experiments with an alkaline solution show that, in this case at least, the resistance film, if it exists at all, does not produce an error of more than 20 millivolts. Oscillograph measurements would most likely prove that the possible error was much smaller than this, as the rate of decay in the first one-hundredth of a second is usually greater than that found afterwards. It is improbable that there is any considerable variation in the mechanism of bubble formation at different electrodes. Further, we should not expect the overvoltage to vary very much on changing the electrolyte, and the overvoltage values obtained by the commutator method with a freshly-amalgamated electrode in alkaline solution approximate to those given by the direct method in acid solution.

We may thus conclude that in all cases the direct method gives very nearly the true value of the overvoltage. The commutator method is incapable of giving accurate results, the error amounting to several tenths of a volt for cathodes with acid electrolyte and being especially large for the mercury cathode in acids.

Summary.

(1) A description is given of a remarkable phenomenon depending on the change of surface tension with potential at a mercury electrode.

(2) The overvoltages at cathodes of mercury and amalgamated lead have been measured by the direct method and by the commutator method.

(3) These experiments show that the direct method gives the more accurate results.

The author's thanks are due to Professor Sir James Walker for helpful advice in the presentation of this paper.

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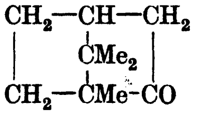
[*Received, May 6th,* 1921.]

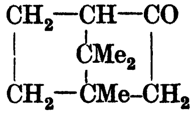
CXX.—*Epicamphor. Part II.*

By WILLIAM HENRY PERKIN, jun., and ALAN FRANCIS TITLEY.

THE relationship of camphor to epicamphor is that represented by the formulæ:



Camphor.



Epicamphor.

and since the first published account of the preparation of epicamphor (Lankshear and Perkin, P., 1911, **27**, 167), this substance has been the subject of an extended investigation (Bredt and Perkin, T., 1913, **103**, 2182) which had for its object the discovery of the best conditions for the preparation and the study of the more important derivatives of this interesting substance. One unexpected observation, established in the early stages of the work, was that the conversion of camphor into epicamphor results in the reversal of the sign of rotation, the opposite change taking place, of course, when epicamphor is converted into camphor, and this important point may be summarised thus:

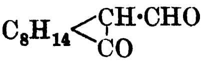
d-Camphor, $[\alpha]_D + 39{\cdot}1^\circ \rightleftharpoons$ *l*-Epicamphor, $[\alpha]_D - 58{\cdot}2^\circ$
(m. p. 175°) (m. p. 182°)

At a later date, Furness and Perkin (T., 1914, **105**, 2025) completed the epicamphor series by converting *l*-camphor into *d*-epicamphor ($[\alpha]_D + 58{\cdot}4^\circ$) and the mixture of *d*- and *l*-epicamphor yielded *dl*-epicamphor, which melts at 180°. The communication of Bredt and Perkin (*loc. cit.*) contains the description of a large number of derivatives of *l*-epicamphor, which need not be enumerated here, but certain important derivatives were not prepared at that time, and it is the purpose of the present communication to deal briefly with two of these, namely, ***hydroxymethylene*-l-*epicamphor*** and l-*epicampholenonitrile.*

I. *Hydroxymethylene*-l-*epicamphor.*

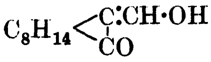
Hydroxymethylene-*d*-camphor is obtained by acting on *d*-camphor with sodium and *iso*amyl formate in the presence of ether, and has been extensively investigated by Bishop, Claisen, and Sinclair

(*Annalen*, 1894, **281**, 314), Brühl (*Zeitsch. physikal. Chem.*, 1900, **34**, 31), Federlin (*Annalen*, 1907, **356**, 251), and by Pope and Read (T., 1909, **95**, 171). The first-named pointed out that three constitutional formulæ are possible for hydroxymethylenecamphor, namely:



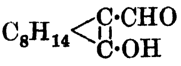
$C_8H_{14}<\begin{matrix}CH\cdot CHO\\ CO\end{matrix}$

(I).



$C_8H_{14}<\begin{matrix}C{:}CH\cdot OH\\ CO\end{matrix}$

(II.)

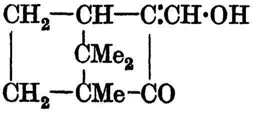


$C_8H_{14}<\begin{matrix}C\cdot CHO\\ \|\\ C\cdot OH\end{matrix}$

(III.)

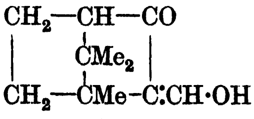
The refractometric examination of methyl-alcoholic and chloroform solutions of hydroxymethylenecamphor by Brühl and the investigation by Federlin of the colour intensity (reddish-violet) produced by ferric chloride in different solvents, measured directly and after standing, seem to indicate that the substance is not the keto-aldehyde (I), but is, in all probability, constituted as represented by (II), and this also was the opinion of Bishop, Claisen, and Sinclair. For these and other reasons, this type of formula has been adopted in the present communication, although, as Pope and Read (*loc. cit.*, p. 175) have pointed out, neither the refractometric nor the colorimetric method lends itself to differentiating between the two enolic modifications (II) and (III). One of the most characteristic properties of hydroxymethylenecamphor is the observation of Pope and Read that this substance exhibits marked mutarotation.

A freshly-prepared solution in alcohol had $[\alpha]_D+201\cdot8°$, but this had diminished to $+186\cdot0°$ in seventy-two hours; the change is even more marked in benzene solution, the initial rotation of $+169\cdot5°$ decreasing to $+80\cdot8°$ in twenty days. These as well as other remarkable properties of hydroxymethylenecamphor made it very desirable to prepare and investigate hydroxymethylene-epicamphor, and indeed there is sufficient difference between the formulæ of the two substances



Hydroxymethylenecamphor.

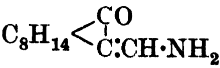
and



Hydroxymethylene-epicamphor.

—containing, as they do, the dissimilar reactive groupings, $>CH\cdot C{:}CH\cdot OH$ and $>CMe\cdot C{:}CH\cdot OH$—to make it probable that the two substances might exhibit widely differing properties. This has, in fact, been found to be the case. *Hydroxymethylene*-l-*epicamphor* is readily prepared from *l*-epicamphor by treatment with *iso*amyl formate and sodium in the presence of ether; it is readily volatile in steam, melts at 89°, and gives a violet coloration when ferric chloride is added to its alcoholic solution. It exhibits mutarotation to a slight extent only, and that in an opposite sense to the mutarotation of hydroxymethylenecamphor, for, whereas the rotation of the solutions of the latter decreases very markedly on keeping, the rotation of solutions of hydroxymethylene-epicamphor increases somewhat on standing, and especially when a trace of sodium ethoxide is added. Thus, if hydroxymethylene-epicamphor is steam distilled, rapidly dried, and dissolved in benzene, the solution has $[\alpha]_D$ $-125{\cdot}5°$, and this value rises to $-130{\cdot}5°$ after twenty-four hours.

If the specimen examined has been kept for a fortnight and is then dissolved in benzene, the initial rotation is $-131{\cdot}1°$, and this rises to $-134{\cdot}4°$ in seven days. A specimen three weeks old gave, in alcohol, $[\alpha]_D$ $-138{\cdot}8°$, and this rose to $-139{\cdot}5°$ in ten hours; when, however, the alcoholic solution of this specimen was mixed with a trace of sodium ethoxide, the immediate rotation was $-146{\cdot}7°$, and this had not changed at the end of twenty-four hours. Another striking difference in the hydroxymethylene derivatives of camphor and epicamphor is the fact that, whereas the former, as is well known, soon becomes yellow and viscous on standing, this change is very much less marked in the case of the epicamphor derivative. In some other respects, the two hydroxymethylene derivatives exhibit considerable similarity. *Benzoyloxymethylene-epicamphor* melts at 106° and the *semicarbazone* of *hydroxymethylene-epicamphor* at 197°, and these closely resemble the corresponding camphor derivatives, which melt at 120° and 219° respectively. Hydroxymethylenecamphor combines readily with amines with elimination of water, the grouping $>C{:}CH{\cdot}OH$ being changed to $>C{:}CH{\cdot}NHR$, and several of these condensation products have been investigated by Pope and Read (*loc. cit.*, p. 177). The optical properties of some of these substances are so remarkable that it was decided, in order to enable comparison to be made, to prepare the corresponding derivatives from hydroxymethylene-epicamphor.

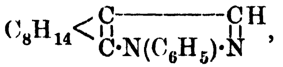
Aminomethylene-l-*epicamphor*,  $C_8H_{14}{<}\begin{matrix}CO\\ |\\ C{:}CH{\cdot}NH_2\end{matrix}$, obtained by heating hydroxymethylene-epicamphor with aqueous ammonia, does not exhibit mutarotation, since, in benzene solution, the initial value, $[\alpha]_D$ $-296{\cdot}9°$, does not change after twenty-four hours. On the other hand, we have found that aminomethylene-*d*-camphor exhibits marked mutarotation, a fact which does not appear to have been previously observed. In one experiment, the solution in benzene, examined immediately, had $[\alpha]_D$ $+300{\cdot}8°$, and this value dropped to $+218{\cdot}6°$ in a week.

Anilinomethylene-l-*epicamphor*, $C_8H_{14}<\begin{smallmatrix}CO\\ \mid\\ C{:}CH\cdot NH\cdot C_6H_5\end{smallmatrix}$, crystallises in needles, melts at 101° and does not exhibit mutarotation, since the value in benzene solution, $[\alpha]_D$ $-271{\cdot}5°$, did not change appreciably during twenty-four hours.

Anilinomethylene-*d*-camphor melts at 167—170° and exhibits slight mutarotation, the value in benzene solution diminishing from $[\alpha]_D$ $+309{\cdot}4°$ to $+273{\cdot}1°$ in twenty hours (Pope and Read, *loc. cit.*, p. 177).

β-*Naphthylaminomethylene*-l-*epicamphor*, $C_8H_{14}<\begin{smallmatrix}CO\\ \mid\\ C{:}CH\cdot NH\cdot C_{10}H_7\end{smallmatrix}$, was prepared because Pope and Read (*loc. cit.*, p. 178) had observed that β-naphthylaminomethylene-*d*-camphor (m. p. 187°) exhibited mutarotation to a remarkable degree; the solution in benzene gave, at first, $[\alpha]_D$ $+264{\cdot}6°$, whereas after twenty-four hours, this had diminished to $+10{\cdot}1°$. β-*Naphthylaminomethylene*-l-*epicamphor* melts lower, namely, at 110° and has, in benzene solution, $[\alpha]_D$ $-202{\cdot}5°$, a value which rises to $-222{\cdot}5°$ in twenty-four hours, so that the mutarotation is not only slight but in the reverse direction to the striking mutarotation of the camphor derivative.

Perhaps the most remarkable difference exhibited by the hydroxymethylene derivatives of camphor and epicamphor is in their behaviour towards phenylhydrazine. Bishop, Claisen, and Sinclair (*Annalen*, 1894, **281**, 352) made the observation that hydroxymethylenecamphor combines very readily with phenylhydrazine to yield the phenylpyrazole,



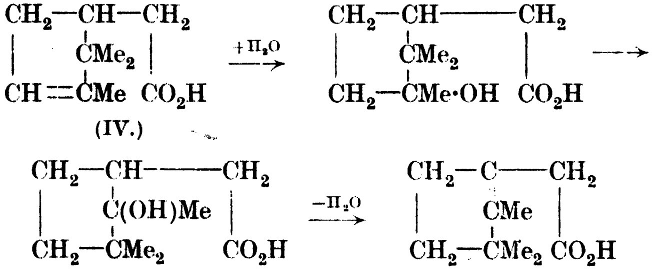
$$C_8H_{14}<\begin{matrix}C & \text{———} & CH\\ \| & & \|\\ C\cdot N(C_6H_5) & \cdot & N\end{matrix},$$

when the substances are mixed in acetic acid solution and heated on the steam-bath. In the case of hydroxymethylene-epicamphor, we were unable to bring about this condensation, the hydroxymethylene derivative remaining unchanged in circumstances which readily led to condensation in the case of the camphor derivative. It is very difficult to understand why there should be this striking difference.

II. *Epicampholenonitrile and Epicampholenic Acid.*

Probably no series of changes in the camphor group are more interesting or have been found more difficult of interpretation than the conversion of camphoroxime into α-campholenonitrile and α-campholenic acid, followed by the change of this acid into β-campholenic acid. Nägeli (*Ber.*, 1884, **17**, 805) and, almost at the same time, Goldschmidt and Zurrer (*ibid.*, p. 2070) first showed that camphoroxime is converted by the action of dilute acids into (α-)campholenonitrile, and they prepared the acid by prolonged hydrolysis of the nitrile.

The whole subject was reinvestigated and much extended by Tiemann (*Ber.*, 1895, **28**, 1079, 2166; 1896, **29**, 2613, 3013; 1897, **30**, 243, 328, 405, 594), who showed that two series of campholenic derivatives must be recognised, which he designated α- and β-, the former being optically active, whilst the latter are not. Tiemann's study of the oxidation products of α- and β-campholenic acid, combined with the elucidation of the structure of camphor, finally led to the configurations (IV) and (V) respectively for these acids. Several investigators have shown that in general α-campholenic derivatives may be converted into the β-analogues by the action of strong mineral acids, and the mechanism of the change is generally represented as follows :



$$\begin{array}{l} \mathrm{CH_2—CH—CH_2} \\ |\quad \mathrm{CMe_2} \quad | \\ \mathrm{CH{=}CMe\quad CO_2H} \end{array} \xrightarrow{+\mathrm{H_2O}} \begin{array}{l} \mathrm{CH_2—CH——CH_2} \\ |\quad \mathrm{CMe_2} \quad | \\ \mathrm{CH_2—CMe{\cdot}OH\quad CO_2H} \end{array} \longrightarrow$$

(IV.)

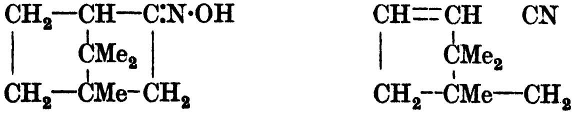
$$\begin{array}{l} \mathrm{CH_2—CH——CH_2} \\ |\quad \mathrm{C(OH)Me} \quad | \\ \mathrm{CH_2—CMe_2\quad CO_2H} \end{array} \xrightarrow{-\mathrm{H_2O}} \begin{array}{l} \mathrm{CH_2—C——CH_2} \\ |\quad \mathrm{CMe} \quad | \\ \mathrm{CH_2—CMe_2\quad CO_2H} \end{array}$$

(V.)

α-Campholenic acid is an oil, distils at 163°/30 mm., and has $[\alpha]_D$ +10·9°, whereas β-campholenic acid melts at 52° and is inactive.

The remarkable series of changes which lead to the formation of the α- and β-campholenic acids made it desirable to ascertain whether similar changes are capable of realisation in the epicamphor series and we have investigated this complex matter as completely as the difficulty of obtaining sufficient quantities of *l*-epicamphor allowed, but we recognise that our results are far from complete.

The decomposition of *l*-epicamphoroxime by dilute sulphuric acid proceeds in a similar manner to that of camphoroxime :



$$\begin{array}{l} \mathrm{CH_2—CH—C{:}N{\cdot}OH} \\ |\quad \mathrm{CMe_2} \quad | \\ \mathrm{CH_2—CMe—CH_2} \end{array} \qquad \begin{array}{l} \mathrm{CH{=}CH\quad CN} \\ |\quad \mathrm{CMe_2} \\ \mathrm{CH_2—CMe—CH_2} \end{array}$$

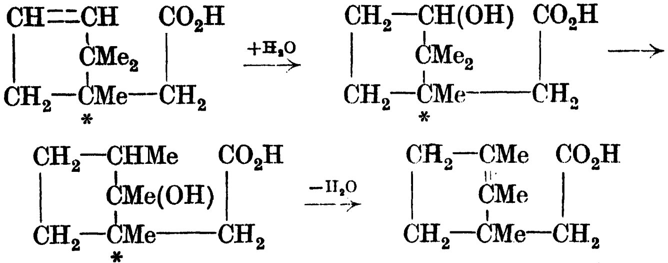
Epicamphoroxime. *Epicampholenonitrile* (VI.)

and the l-*epicampholenonitrile* obtained is an oil very similar to α-campholenonitrile in odour and in physical properties. It distils at 145°/100 mm., has $[\alpha]_D$ −27·4°, and is hydrolysed to l-α-*epicampholenic acid* with even greater difficulty than in the case of the hydrolysis of α-campholenonitrile to the corresponding acid.

l-α-*Epicampholenic acid* is an oil, distils at 166°/30 mm., and has $[\alpha]_D$ −38·4°.

Attempts to Prepare β-Epicampholenonitrile.

The conversion of α-campholenic acid into β-campholenic acid is illustrated above, and there seemed no reason why a similar process might not be realisable in the epi-series and result in the formation of β-epicampholenic acid, thus :

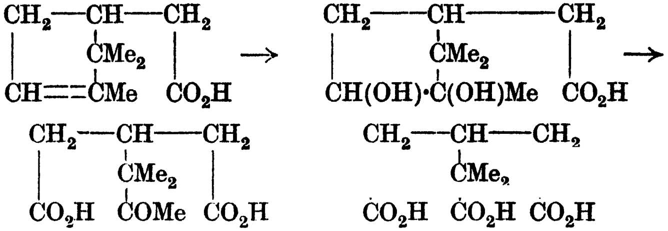


β-Epicampholenic acid.

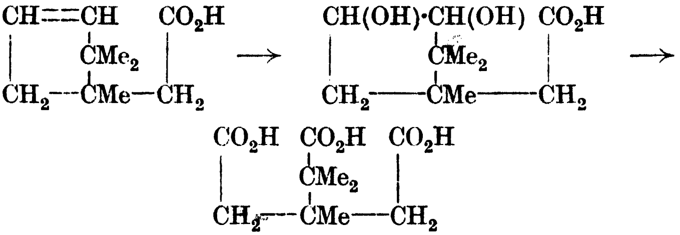
One difference in the two parallel intramolecular series of changes is at once obvious, namely, that, whereas the conversion of α-campholenic acid into the β-acid involves the disappearance of the asymmetric carbon atom and consequent loss of optical activity, this is not the case in the epi-series and therefore the α- and β-epicampholenic acids should both be optically active. In the hope of obtaining β-epicampholenic acid, epicamphoroxime was heated with hydriodic acid (D 1·7) for six hours and the nitrile produced was distilled, when it was found to have all the properties of the α-nitrile, that is, it distilled at 144—145°/100 mm. and had $[\alpha]_D$ −26·6°. Other experiments, which need not be described in detail, did not give any indication of the formation of a β-isomeride, and it is clear that β-epi-derivatives are not produced under conditions which so readily lead to the formation of β-campholenic derivatives.

Oxidation of Epicampholenic Acid.

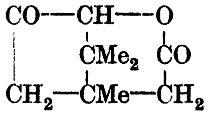
α-Campholenic acid is characterised by the ease with which it breaks down on oxidation, yielding acids which furnish a clear proof of its constitution. Thus, when oxidised with permanganate, it is converted into dihydroxydihydro-α-campholenic acid, which, on further oxidation with chromic acid, yields *iso*ketocamphoric acid and *iso*camphoronic acid :



It seemed probable that the oxidation of epicampholenic acid would follow a similar course and yield dihydroxydihydroepicampholenic acid and methyl*iso*camphoronic acid :



Experiment showed, however, that this oxidation takes an unexpected course, and further work will be necessary before the mechanism of the degradation can be understood. During the oxidation of epicampholenic acid with permanganate, a beautifully crystalline lactone is formed, which melts at 80° and has $[\alpha]_D$ +45·8°. There can be little doubt that this substance is the *lactone* of *hydroxyketodihydroepicampholenic acid* and has either the constitution



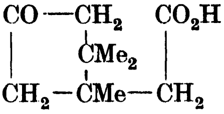
(VII.)

or more probably, since the lactone does not combine with semicarbazide, the tautomeric formula containing the grouping -CH:C(OH)-. The main products of the oxidation were syrupy acids which could not be obtained crystalline, and from the syrup an ester was prepared which distilled at 150—155°/10 mm., had $[\alpha]_D$ +34·4° and, on hydrolysis, gave a syrupy ketonic acid (*A*), which yielded a semicarbazone, $C_{11}H_{19}O_3N_3$, melting at 203°.

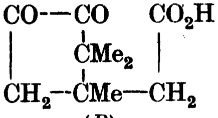
The mixture of syrupy acids from the permanganate oxidation was oxidised by chromic acid and the product esterified, when an ester, $C_{12}H_{18}O_4$, was obtained which distilled at 185°/30 mm.

and, on hydrolysis, yielded an optically active, monobasic acid, $C_{10}H_{14}O_4$ (*B*), ($[\alpha]_D$ +28·9°).

The semicarbazone of this acid, $C_{11}H_{17}O_4N_3$, crystallises well and melts at 168°. It is probable that the acids (*A*) and (*B*) have the constitutional formulæ:

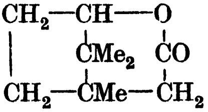


(*A*)

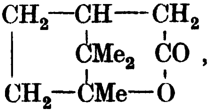


(*B*)

The following additional facts were ascertained during the investigation of epicampholenic acid. When epicamphoroxime is boiled with dilute acids, besides epicampholenic acid, a lactone, $C_{10}H_{16}O_2$, is produced, which is a syrup, distils at 168°/30 mm. and has $[\alpha]_D$ −3·47°. There can be no doubt that this is *dihydroepicampholenolactone* (*C*),

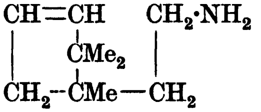


(*C*)

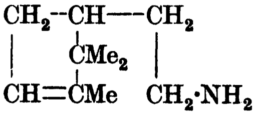


(*D*)

and corresponds with dihydrocampholenolactone (*D*) obtained by Tiemann (*Ber.*, 1897, **30**, 329) from the product of the action of mineral acids on camphoroxime. We have also prepared l-*epicamphylamine*, by the reduction of epicampholenonitrile with sodium and alcohol; this base distils at 128°/100 mm., has $[\alpha]_D$ +17·6°, and readily absorbs carbon dioxide from the air. This interesting base is obviously the counterpart in the epicamphor series of camphylamine, which Tiemann (*Ber.*, 1896, **29**, 3008) obtained from α-campholenonitrile by reduction with tin and hydrochloric acid.



Epicamphylamine (VIII.).



Camphylamine.

EXPERIMENTAL.

Hydroxymethylene-l-*epicamphor.*

Sodium (3 grams), granulated by melting under xylene and shaking vigorously, is washed with dry ether until free from xylene and then a solution of *l*-epicamphor (13 grams) in dry ether (80 c.c.) is added.

The flask is connected with a reflux condenser, the whole thoroughly cooled in ice and salt, and freshly distilled *iso*amyl formate (17 grams) slowly added through a tap-funnel. If the reaction does not start, the flask is warmed with the hand; it then proceeds evenly, enough heat being developed to keep the ether boiling. After twenty-four hours, the brown, viscid product is mixed with ice water (100 c.c.), the aqueous layer separated, and twice extracted with ether in order to free it completely from epiborneol and unchanged epicamphor. The dissolved ether is removed by passing air through the solution, which is then well cooled with ice, and 30 per cent. acetic acid added until no more oil separates. The oil soon solidifies and is collected, left in contact with porous porcelain until free from oil, and distilled in steam, when pure *hydroxymethylene-epicamphor* passes over as a colourless oil which soon solidifies to a crystalline mass. After draining on porcelain and drying in a vacuum desiccator over sulphuric acid, the following analysis was made: Found: C=73·2; H=8·9. $C_{11}H_{16}O_2$ requires C=73·3; H=8·9 per cent.

Hydroxymethylene-l-*epicamphor* melts at 89° and has only a faint odour; it is readily soluble in the ordinary organic solvents and slightly soluble in hot water. Claisen (*Annalen*, 1894, **281**, 314) observed that colourless hydroxymethylenecamphor gradually passes into a yellow, viscous modification, and hydroxymethylene-epicamphor exhibits a somewhat similar behaviour and also becomes amorphous. The change, however, is slower than in the case of the camphor derivative. A benzene solution of hydroxymethylene-epicamphor only slowly assumes a yellow colour when exposed to light, whereas a hydroxymethylenecamphor solution of equal concentration becomes a much deeper yellow in a shorter time.

Optical Rotation of Hydroxymethylene-l-*epicamphor.*

Hydroxymethylene-l-*epicamphor* is lævorotatory and its mutarotation, although apparently real, is only slight compared with that exhibited by the camphor derivative.

The following three sets of measurements were made.

Specimen freshly steam-distilled.

Weight in 20 c.c. of benzene. Gram.	Time.	α_D.	$[\alpha]_D$.
0·1694	0	−2·11°	−124·5°
,,	1 hour	−2·19	−129·2
,,	2 ,,	−2·21	−130·5
,,	6 ,,	−2·21	−130·5
,,	24 ,,	−2·21	−130·5

Specimen about a fortnight old.

Weight in 20 c.c. of benzene. Gram.	Time.	α_D.	$[\alpha]_D$.
0·1518	0	−2·09°	−131·1°
,,	1 hour	−2·13	−133·7
,,	3 ,,	−2·13	−133·7
,,	24 ,,	−2·13	−133·7
,,	1 week	−2·14	−134·4

Specimen about three weeks old (in alcohol).

Weight in 20 c.c. of alcohol. Gram.	Time.	α_D.	$[\alpha]_D$.
0·0852	0	−1·18°	−138·8°
,,	1 hour	−1·18	−138·8
,,	18 ,,	−1·19	−139·5

After the addition of a trace of sodium ethoxide.

Gram.	Time.	α_D.	$[\alpha]_D$.
0·0852	0	−1·25	−146·7°
,,	24 hours	−1·25	−146·7

Pope and Read (T., 1909, **95**, 175) found that hydroxymethylenecamphor was dextrorotatory and that the rotation decreased markedly with time.

The following is a typical set of the results that they obtained.

Weight in 25 c.c. of benzene. Gram.	Time.	α_D.	$[\alpha]_D$.
0·1563	0	+2·12°	+169·5°
,,	2 hours	+1·63	+130·4
,,	9 ,,	+1·15	+ 92·0
,,	36 ,,	+1·10	+ 88·0
,,	20 days	+1·01	+ 80·8

The change is rather less in alcohol.

The mutarotation is thus in the opposite sense to that shown by the epicamphor derivative, and it appears that in the case of the latter the conversion of one tautomeric form into the other takes place only very slowly.

An alcoholic solution of hydroxymethylene-epicamphor gives a violet colour with ferric chloride, and reduces an ammoniacal solution of silver nitrate, with formation of a silver mirror. An attempt was made to apply the latter reaction in order to get an approximate idea of the relative amounts of the aldehyde form present at equilibrium in alcoholic solutions of the camphor and epicamphor derivatives.

Equal weights (0·15 gram) of the two substances, both freshly steam-distilled, were placed in two similar, well-cleaned test-tubes and dissolved in equal weights of alcohol. Equal volumes of the same solution of (approximately decinormal) ammoniacal silver nitrate were then added from two burettes, and the two solutions allowed to stand at room temperature. The solution of the camphor derivative became dark at once, but that of the epi-derivative did not change appreciably for a considerable time. After one hour, the former had deposited a complete mirror, while the latter had merely become dark in colour. After three and a half hours, the latter had also deposited a uniform mirror.

Since it may be assumed that, in the presence of the ammonia, the equilibrium mixture, in both cases, is attained very rapidly, the rate of reduction should be proportional to the concentration of the aldehyde form, present at equilibrium.

The results appear to show that considerably more conversion into the aldehyde form takes place in solutions of the camphor than of the epicamphor derivative.

It is possible that the comparative stability of the crystalline form of the epi-derivative and the slowness of colour change in its solutions are related phenomena.

Benzoyloxymethylene-epicamphor.

Hydroxymethylene-epicamphor (0·5 gram) was dissolved in 5 grams of 10 per cent. sodium hydroxide, and 0·6 gram of benzoyl chloride added. The benzoyl derivative separated on shaking as a pasty, white mass, quickly becoming powdery. It crystallised from high-boiling light petroleum in glittering plates which melted at 105—106° (Found: C=75·82; H=7·11. $C_{18}H_{20}O_3$ requires C=76·05; H=7·04 per cent.).

The corresponding camphor derivative melts at 119—120°.

Hydroxymethylene-epicamphorsemicarbazone.

Hydroxymethylene-epicamphor (0·5 gram) was dissolved in 80 per cent. alcohol, semicarbazide hydrochloride (0·4 gram) and excess of sodium acetate added, and the whole digested on the water-bath for an hour. On diluting with water, the semicarbazone did not separate, but by slowly evaporating off the alcohol, it was deposited in faintly yellow flakes. The substance crystallised from hot alcohol in almost colourless, very small needles which melted with decomposition at 196—197° (Found: N=17·4. $C_{12}H_{19}O_2N_3$ requires N=17·7 per cent.).

The corresponding camphor derivative melts at 219° and is almost insoluble in hot alcohol.

Anilinomethylene-epicamphor.

This condensation product was obtained as a rather oily precipitate when a solution of hydroxymethylene-epicamphor in methyl alcohol was mixed with the equivalent quantity of aniline dissolved in 30 per cent. acetic acid. Recrystallised from light petroleum of high b. p., it formed small, faintly yellow needles which melted at 101° (Found : N=5·50. $C_{17}H_{21}ON$ requires N=5·49 per cent.).

This substance does not show an appreciable mutarotation, as the following figures prove.

Weight in 20 c.c. of benzene. Gram.	Time.	α_D.	$[\alpha]_D$.
0·0685	0	−1·86°	−271·5°
,,	2 hours	−1·84	−268·6
,,	6 ,,	−1·84	−268·6
,,	24 ,,	−1·84	−268·6

Pope and Read (*loc. cit.*, p. 177) found that the corresponding derivative of camphor had a small mutarotation.

They obtained : Time 0, $[\alpha]_D$ +309·4°; 24 hours, $[\alpha]_D$ +273·1°.

β-*Naphthylaminomethylene-epicamphor.*

This substance was prepared because Pope had shown that β-naphthylaminomethylenecamphor exhibited a very marked mutarotation.

It separates at once as a copious crystalline precipitate when an alcoholic solution of hydroxymethylene-epicamphor is mixed with the corresponding quantity of β-naphthylamine dissolved in 30 per cent. acetic acid.

On recrystallisation from alcohol, pale yellow, silky needles were obtained, melting at 109—110° (Found : C=82·6; H=7·4; N=4·6. $C_{21}H_{23}ON$ requires C=82·6; H=7·5; N=4·6 per cent.).

Pope and Read (*loc. cit.*, p. 178) found that the corresponding camphor derivative (m. p. 184—187°) exhibited a curious phenomenon. They state that "on dissolving 0·16 gram of the substance in 20 c.c. of benzene with the aid of heat and allowing to cool, the colourless solution deposits a white, crystalline material; this, however, immediately redissolves, yielding a reddish-brown solution."

β-Naphthylaminomethylene-epicamphor does not show this behaviour.

For the mutarotation of β-naphthylaminomethylenecamphor they obtained the following remarkable figures:

Time 0, $[\alpha]_D$ +264·6°. After 24 hours, $[\alpha]_D$ +10·1°.

The following values for the mutarotation of β-naphthylaminomethylene-epicamphor were obtained.

Weight in 20 c.c. of benzene. Gram.	Time.	α_D.	$[\alpha]_D$.
0·1200	0	−2·43°	−202·5°
,,	2 hours	−2·46	−205·0
,,	6 ,,	−2·64	−220·0
,,	24 ,,	−2·67	−222·5
,,	5 days	−2·67	−222·5

Weight in 20 c.c. of alcohol (with trace of NaOEt). Gram.	Time.	α_D.	$[\alpha]_D$.
0·1153	0	−2·54°	−220·3°
,,	1 hour	−2·59	−224·6
,,	6 hours	−2·62	−227·2

The benzene solution, when left in the light with a free air space above it, gradually acquires a reddish-brown colour. If kept away from the light, however, it remains practically unchanged over a long period.

Aminomethylene-epicamphor.

The amino-derivative can be readily obtained by heating hydroxymethylene-epicamphor with five times its weight of aqueous ammonia (0·880) in a sealed tube at 100° for four to five hours.

It forms a faintly yellow, crystalline mass, which crystallises from light petroleum in colourless needles melting at 122° (Found: N=7·8. $C_{11}H_{17}ON$ requires N=7·8 per cent.).

0·1064 Gram made up to 20 c.c. in benzene gave α_D −3·16°, whence $[\alpha]_D$ −296·9°, and the same value after twenty-four hours.

The mutarotation of aminomethylenecamphor, which does not appear to have been previously investigated, was measured. It is fairly large and is of some interest, as the compound can be regarded as the simplest member of the various amino-derivatives investigated by Pope and Read.

The specimen prepared melted at 155—156° and gave the following values:

Weight in 20 c.c. of benzene. Gram.	Time.	α_D.	$[\alpha]_D$.
0·0924	0	+2·78°	+300·8°
,,	2 hours	+2·48	+268·4
,,	24 ,,	+2·11	+228·3
,,	1 week	+2·02	+218·6

Bishop, Claisen, and Sinclair (*Annalen*, 1894, **281**, 352) found that hydroxymethylenecamphor condensed with phenylhydrazine in acetic acid solution to give a phenylpyrazole (see p. 1092), reaction taking place between the phenylhydrazine and the aldehyde form of hydroxymethylenecamphor.

It is a curious fact that all attempts to obtain the corresponding phenylpyrazole from the epi-derivative failed.

No such condensation took place, either in acetic acid solution or when the dry materials were heated together, although check experiments with corresponding quantities of the camphor derivative confirmed Claisen's result and gave a nearly quantitative yield of the pyrazole in every case.

The negative result is explicable if it is assumed that only the aldehyde form can condense, and that none of this form is present in the acid solution. It is difficult to conceive, however, why the ketonic form itself should not react readily with phenylhydrazine.

l-*Epicampholenonitrile* (Formula VI).

In preparing this substance, 15 grams of epicamphoroxime (compare T., 1913, **103**, 2208) are added to 100 c.c. of 20 per cent. sulphuric acid, and the mixture heated for two to three hours on the water-bath. The oxime dissolves fairly rapidly and oily drops separate. After two hours there is an upper layer of oil, and the solution clouds on cooling. The oil is extracted with ether, the ethereal solution washed with dilute sodium carbonate solution, and dried over potassium carbonate.

On fractionation, almost the whole quantity distils at 145—146°/100 mm. as a colourless, strongly refracting oil, with a smell similar to that of campholenonitrile.

2·0847 Grams made up to 20 c.c. in ethyl acetate gave α_D $-5·05°$, whence $[\alpha]_D$ $-24·2°$.

If the material is contaminated, as is probable, with epicamphoroxime, this rotation value will be too low, because l-epicamphoroxime is dextrorotatory. Any oxime can be removed by shaking the oil (not the ethereal solution) with dilute sulphuric acid; after thorough shaking with several fresh quantities of dilute acid, drying, and redistilling, it was found that 1·7308 grams in 20 c.c. of ethyl acetate gave α_D $-4·75°$, whence $[\alpha]_D$ $-27·4°$.

Since further washing did not raise the value of the rotation, the latter is probably a good approximation to the true value.

Epicampholenonitrile boils at 145°/100 mm. and at 214°/754 mm. (Found: C=80·1; H=10·2; N=9·2. $C_{10}H_{15}N$ requires C=80·5; H=10·1; N=9·4 per cent.).

The density of the nitrile was found to be 0·921/15° compared with water at the same temperature, and the refractive index n_D 1·4732.

α-Campholenonitrile boils at 226—227°/760 mm. and 152—153°/100 mm. and has $[\alpha]_D$ +7·3°, n_D 1·4665 and *d* 0·910.

d-*Epicampholenonitrile.*

This *d*-nitrile was similarly prepared, starting from *d*-epicamphoroxime. It distilled at 146—147°/100 mm.

0·7226 Gram made up to 20 c.c. in ethyl acetate gave α_D +1·89°, whence $[\alpha]_D$ +26·2°.

l-*Epicampholenic Acid.*

It has often been observed that α-campholenonitrile is extremely difficult to hydrolyse, and this difficulty is even more pronounced in the case of the epi-derivative.

Five grams of the nitrile were heated for three days under reflux with alcoholic potassium hydroxide, when, on adding water, the nitrile separated practically unchanged and distilled at 146—148°/100 mm.

In this respect it differs markedly from α-campholenonitrile, which is largely converted to the amide by hydrolysis for six hours under these conditions.

The nitrile was then heated for ten days in a sealed tube at 100° with a large excess of methyl-alcoholic potassium hydroxide. The solution smelt strongly of ammonia and hydrolysis appeared to be complete, since on adding water, except for a slight milkiness, nothing separated. The alkaline solution was extracted with ether to remove any nitrile or amide and then evaporated with water until free from methyl alcohol. On acidifying, the acid separated as an extremely viscous, yellow oil, which was extracted with ether and dried over calcium chloride.

The material so obtained may be contaminated with *oxydihydroepicampholenic acid* (compare Tiemann, *Ber.*, 1895, **28**, 1079, 2076) and almost certainly with *dihydroepicampholenolactone* (see below).

The crude material was warmed for a short time with dilute sulphuric acid, to convert any hydroxy-acid present into lactone and then taken up with ether, and the ethereal solution was dried and saturated with dry ammonia. The ammonium salt separated at once in the form of thin, white leaflets, which were extremely hygroscopic, and was filtered off and decomposed with dilute sulphuric acid.

The acid so obtained is a colourless, rather viscous oil distilling at 166°/30 mm. or 181°/100 mm. (Found: C=70·9; H=9·6. $C_{10}H_{16}O_2$ requires C=71·4; H=9·5 per cent.).

0·8542 Gram in 20 c.c. of ethyl acetate gave α_D −3·38°, whence $[\alpha]_D$ −38·4°.

Campholenic acid boils at 258—260° or at 163°/30 mm. and has $[\alpha]_D$ +10·9° (van Kregten, *Rec. trav. chim.*, 1916, **36**, 64).

d-*Epicampholenic Acid.*

The dextro-acid was obtained by the hydrolysis of the dextronitrile. It had b. p. 164—165°/30 mm. and gave $[\alpha]_D$ +39·2° in ethyl acetate.

Dihydroepicampholenolactone (Formula C).

The whole of the ethereal filtrates, from which the ammonium salt of *l*-epicampholenic acid had been precipitated, was again treated with ammonia to remove the last traces of acid, washed with dilute acid to remove dissolved ammonia, and then dried. On distilling off the ether, an inodorous oil was obtained, which differed greatly from epicampholenic acid in viscosity. It distilled at about 168°/30 mm., but as the quantity of material was small, this cannot be taken as exact (Found: C=70·7; H=9·3. $C_{10}H_{16}O_2$ requires C=71·4; H=9·5 per cent.).

0·7480 Gram in 20 c.c. of ethyl acetate gave α_D −0·26°, whence $[\alpha]_D$ −3·47°.

There can be little doubt that this neutral oil consists of *dihydroepicampholenolactone.*

dl-α-*Campholenic Acid.*

Although the *d*- and *l*-modifications do not crystallise, it was thought possible that the *dl*-modification of epicampholenic acid might be obtained crystalline. In order to ascertain whether this would probably be the case, the behaviour of *dl*-α-campholenic acid, which has not been previously described, was first investigated.

The following new substances were therefore prepared, starting from *l*-camphor.

(1) l-α-*Campholenonitrile*, which had b. p. 153°/100 mm.

(2) l-α-*Campholenic acid,* which had b. p. 155°/20 mm.

(3) dl-α-*Campholenic acid,* which had b. p. 169°/40 mm. and did not crystallise after distillation.

This series of experiments indicated that it was unlikely that *dl*-epicampholenic acid would crystallise, and therefore no attempt was made to prepare the *dl*-modification.

l-*Epicamphylamine* (Formula VIII).

This derivative is fairly readily obtained by reduction of *l*-epicampholenonitrile.

The nitrile (5 grams) was dissolved in ten times its weight of ethyl alcohol and reduced with metallic sodium (5 grams). The slight excess of sodium was decomposed by the addition of ice and, after adding water, the solution was neutralised with dilute hydrochloric acid and unchanged nitrile extracted with ether. The aqueous solution, which contained the hydrochloride of the base, was concentrated to a small bulk, rendered strongly alkaline, and steam distilled. A colourless oil was thus obtained, which had a strong smell, resembling that of a higher aliphatic amine. The yield was about 50 per cent.

l-*Epicamphylamine* boils at 127—128°/100 mm. and absorbs carbon dioxide from the air, with formation of a solid carbonate (Found: C=78·07; H=12·26; N=9·08. $C_{10}H_{19}N$ requires C=78·43; H=12·42; N=9·15 per cent.).

1·2900 Grams made up to 20 c.c. in benzene gave α_D +2·26°, whence $[\alpha]_D$ +17·6°.

The hydrochloride is hygroscopic and very soluble in water. It gradually turns brown on preservation.

The corresponding α-camphylamine boils at 194—196°/760 mm. and has $[\alpha]_D$ +6° (compare Goldschmidt and Schulhof, *Ber.*, 1886, **19**, 708; Tiemann, *Ber.*, 1896, **29**, 3008).

Oxidation of Epicampholenic Acid with Permanganate.

l-Epicampholenic acid (10 grams) was dissolved in dilute sodium carbonate solution and oxidised at 0° with dilute permanganate until the colour just remained, a current of carbon dioxide being passed the whole time. The product was then warmed at about 60°, filtered, and the filtrate and washings of the manganese precipitate concentrated to a small bulk on the water-bath. On saturating the yellow, alkaline solution with ammonium sulphate, a colourless substance (*K*) separated in very small needles. After filtering from this and extracting with ether, the filtrate was acidified with dilute hydrochloric acid, when a very viscous, pale yellow oil was deposited, which was extracted with ether and the extract dried over calcium chloride. After evaporating, about 6 grams of a pale yellow syrup remained, which showed no signs of crystallisation after remaining several days in a vacuum over sulphuric acid at 0°.

0·2420 Gram made up to 20 c.c. in benzene gave α_D +4·60°, whence $[\alpha]_D$ +190·1°.

The acid was then converted into the ethyl ester by boiling with ethyl alcohol and sulphuric acid and this ester distilled at 150—155°/10 mm. and had $[\alpha]_D$ +34·4° in acetone, whilst the analytical results indicated that it consisted mainly of the monoketonic ester.

The ester was then hydrolysed with dilute methyl-alcoholic potassium hydroxide, the acid being recovered as a very viscous gum, which, however, did not crystallise. When the sodium salt was treated with an excess of semicarbazide hydrochloride and warmed, a semicarbazone separated in brown flakes which were contaminated by traces of oily material. After filtering, washing with dilute sodium carbonate solution, and recrystallising from alcohol, it melted at 202—203° with decomposition (Found: C=54·74; H=7·69. The semicarbazone of the monoketonic acid [$C_{11}H_{19}O_3N_3$, p. 1096] requires C=54·77; H=7·88 per cent.).

The substance (*K*), which had separated from the alkaline solution after the oxidation with permanganate (see above), was first freed from admixed ammonium sulphate by extraction with chloroform, in which it is very soluble, and, after removing the chloroform in a vacuum, was recrystallised from very dilute alcohol. It formed long needles which melted sharply at 80° (Found: C=65·99; H=7·8. $C_{10}H_{14}O_3$ requires C=65·93; H=7·7 per cent.).

0·2141 Gram in 20 c.c. of ethyl acetate gave α_D +0·96°, whence $[\alpha]_D$ +45·8°.

This *lactone* of *hydroxyketodihydroepicampholenic acid* (formula VII) is volatile in steam and somewhat soluble in water; it is readily soluble in boiling light petroleum, and separates splendidly in long needles like phthalic anhydride. It is insoluble in dilute ammonia, but dissolves readily in sodium hydroxide solution on warming, the clear solution becomes milky on acidifying, and the lactone soon separates in crystals. The solution in dilute sodium hydroxide readily reduces permanganate to manganate. The lactone separates unchanged from the solution in semicarbazide acetate and does not appear to yield an acetyl derivative on boiling with acetyl chloride for half an hour.

Oxidation of the Acid, obtained by the Permanganate Oxidation of l-Epicampholenic Acid, with Chromic Acid.

Eight grams of this crude acid were dissolved in 200 c.c. of warm water and oxidised with 13 grams of potassium dichromate and 20 grams of concentrated sulphuric acid on a boiling-water bath. Oxidation was slow at first, but rather more rapid later and, when cold, the solution was saturated with ammonium sulphate and extracted several times with ether. In this way a brown gum was obtained, which could not be induced to crystallise. The acid was therefore not analysed but converted at once to the ethyl ester, the main fraction of which boiled at 183—185°/30 mm. (Found: C=64·35; H=8·13. The ester, $C_{12}H_{18}O_4$, of the diketo-acid [p. 1096] requires C=63·77; H=7·94 per cent.).

On hydrolysis with hydrochloric acid, the acid was recovered as a viscous, brown gum, which, after standing over calcium chloride for some days in a vacuum, set to a resin, but did not crystallise.

On titration, 1·0135 grams required 0·2076 gram of NaOH for neutralisation, whereas this quantity of the diketo-acid, $C_{10}H_{14}O_4$ (monobasic), should neutralise 0·2047 gram of NaOH.

The acid is optically active; 0·2522 gram in 20 c.c. of ethyl acetate gave $\alpha_D + 0·73°$, whence $[\alpha]_D + 28·9°$.

When the sodium salt of the acid was warmed with an aqueous solution containing a slight excess of semicarbazide hydrochloride the *semicarbazone* separated on cooling in yellow flakes.

After recrystallisation from hot water, it was almost colourless and melted at 168° (Found: C=51·97; H=6·59. The monosemicarbazone, $C_{11}H_{17}O_4N_3$, of the diketo-acid requires C=51·76; H=6·66 per cent.).

An attempt was made to obtain the disemicarbazone by heating the monosemicarbazone with semicarbazide hydrochloride and sodium acetate, but although a small quantity of a substance of higher m. p. (189—191°) was isolated, the amount obtained was not sufficient for analysis.

One of us (A. F. T.) wishes to make acknowledgment to the Royal Commissioners for the Exhibition of 1851 for a scholarship, with the aid of which this research has been carried out.

THE UNIVERSITY CHEMICAL LABORATORIES,
OXFORD.

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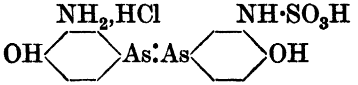
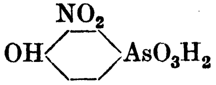
CXXI.—*Derivatives of Sulphur in Commercial Salvarsan. Part I.*

By HAROLD KING.

THE biological testing of commercial samples of salvarsan has revealed the great difficulty which the manufacturers have to face in the variable toxicity of their preparations. The two main factors which contribute to this variation in toxicity, and therefore in homogeneity, are, in the first place, the amorphous or doubtfully crystalline nature of the substance, rendering purification difficult, and, secondly, the use of sodium hyposulphite in the reduction process.

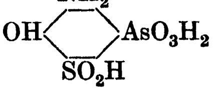
Fargher and Pyman (T., 1920, **117**, 373) made the highly interesting and important observation that methyl-alcoholic solutions of commercial salvarsan deposit a substance which they regarded as the monohydrochloride of the monosulphamic acid of 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene (I).


(I.)


(II.)

They also adduced evidence that the sulphur enters the molecule during the first stage of the reduction process, namely, the reduction of the nitro-group of 3-nitro-4-hydroxyphenylarsinic acid (II) by the hyposulphite, but they state that they were unable to isolate the substance containing sulphur as an arsinic acid.

During the examination of some samples of commercial salvarsan for the Salvarsan Committee of the Medical Research Council the present author came across an abnormal commercial sample which, when dissolved in methyl alcohol, gave a 24 per cent. yield of a substance agreeing analytically with Fargher and Pyman's findings. This seemed to indicate that, under suitable conditions, one ought to find a 10 per cent. yield of the sulphur-substituted phenylarsinic acid in the reduction of the nitrohydroxy-acid. A careful examination was accordingly made of the reduction of 3-nitro-4-hydroxyphenylarsinic acid (II) to the corresponding amino-acid by sodium hyposulphite. The chief reduction products which have so far been found and identified are 3-amino-4-hydroxyphenylarsinic acid as the main product, *3-amino-4-hydroxy-5-sulphinophenylarsinic acid* (III) and its corresponding arseno-derivative, *3 : 3′-diamino-4 : 4′-dihydroxy-5 : 5′-disulphinoarsenobenzene* (IV).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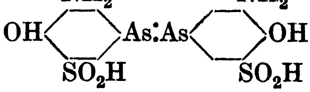
(IV.)

This sulphinic acid * arises constantly under the conditions of the reduction as described in the experimental part, to the extent of 10 grams from 106 grams of the original nitrohydroxy-acid. This in itself would be sufficient to account for the whole of the sulphur content of many specimens of salvarsan. The corresponding disulphinoarseno-derivative arises in much smaller proportions, the amount increasing at the expense of the sulphinoarsinic acid with rise of temperature. There is some evidence of the formation of the mixed arseno-derivative at the same time. The pure sulphinoarsinic acid can be reduced to its corresponding disulphinoarsenobenzene (IV) by sodium hyposulphite, but better by hypophosphorous acid at 100°. The product agrees in its properties with the disulphinoarsenobenzene referred to above and produced in the reduction of nitrohydroxyphenylarsinic acid. The mixed arsenobenzene, 3 : 3′-*diamino*-4 : 4′-*dihydroxy*-5-*sulphinoarsenobenzene monohydrochloride* (V), has been prepared by reduction of an equimolecular

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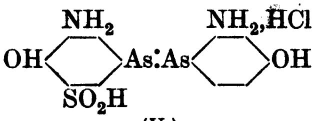
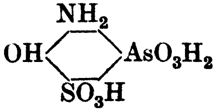
* The possibility that this substance is 3-amino-4-hydroxy-5-sulphophenylarsenious acid seems to be negatived by the analyses of the corresponding arsenobenzenes (IV) and (VII), by the different toxicities of these arsenobenzenes and by the parallelism between the solubility in water of this



(V.)

mixture of the parent aminohydroxyphenylarsinic acid and its 5-substituted sulphinic acid, both by sodium hyposulphite and by hypophosphorous acid. This is the substance which is the main impurity in commercial salvarsan, and represents in a pure form one of the constituents of the substance which Fargher and Pyman first isolated by reason of its sparing solubility in methyl alcohol.

3-Amino-4-hydroxy-5-sulphinophenylarsinic acid, on oxidation with a 3 per cent. solution of hydrogen peroxide in the calculated amount, passes smoothly and without concomitant indophenol formation into 3-*amino*-4-*hydroxy*-5-*sulphophenylarsinic acid* (VI), an acid which has also been isolated by the oxidation of the constituent of salvarsan which is insoluble in methyl alcohol.



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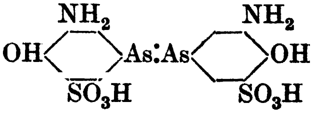

(VII.)

sulphinic acid and the corresponding sulpho-acid (VI), and the solubility in water of aromatic sulphinic and sulpho-acids in general. The solubility of the oxide, on the other hand, might be expected to be greater than that of the sulpho-acid (VI), as its nearest analogue, 3-amino-4-hydroxyphenylarsenious oxide, is more soluble than its corresponding arsinic acid. Experiments on the preparation of 3-amino-4-hydroxy-5-sulphophenylarsenious acid for direct comparison are in progress.

This acid, on reduction with hypophosphorous acid at 55°, gives 3 : 3′ - *diamino* - 4 : 4′ - *dihydroxy*-5 : 5′-*disulphoarsenobenzene* (VII). Reduction of an equimolecular mixture of the sulphonic acid and 3-amino-4-hydroxyphenylarsinic acid with hypophosphorous acid at 60° gave the pure mixed arseno-derivative, 3 : 3′-*diamino*-4 : 4′-*dihydroxy*-5-*sulphoarsenobenzene monohydrochloride*, which may also be a constituent of the substance from salvarsan insoluble in methyl alcohol, whilst a mixture of the sulphonic and sulphinic acids in molecular proportions gave 3 : 3′-*diamino*-4 : 4′-*dihydroxy*-5-*sulpho*-5′-*sulphinoarsenobenzene* on reduction with the same reagent at 100°.

The position of the sulphinic or sulphonic acid group follows from the conversion of 3 : 3′-diamino-4 : 4′-dihydroxy-5 : 5′-disulphoarsenobenzene, by hydrolysis by Karrer's method (*Ber.*, 1915, **48**, 1058), into an o-*aminophenolsulphonic acid,* which differs from the two known *o*-aminophenolsulphonic acids, which contain the sulpho-groups *para* to the amino- or hydroxyl-groups. Experiments designed to fix the position with complete certainty are in progress.

The exclusive formation of a mixed arsenobenzene by the reduction of an equimolecular mixture of phenylarsinic acids, when a mixture of the three arsenobenzenes might be expected, has never been satisfactorily explained. The experiment herein described of the reduction of an equimolecular mixture of 3-amino-4-hydroxy-5-sulphinophenylarsinic acid and 3-amino-4-hydroxyphenylarsinic acid furnishes a clue. When the latter acid is reduced by hypophosphorous acid at 60°, the reagents are in solution throughout and the resulting salvarsan base is isolated by addition of sodium hydrogen carbonate. When the former acid, which is insoluble in water, is reduced by hypophosphorous acid at 100°, reduction to the arsenobenzene, which is also insoluble in this medium, takes place through the medium of the solvent by virtue of the small solubility of the arsinic acid. When the equimolecular mixture of the two acids, one of which is soluble, the other insoluble, is reduced, there is a quantitative formation and separation from the solution of the pure, insoluble, mixed arseno-derivative. It is evident that the controlling factor is the smaller solubility of the mixed arsenobenzene. It is probable that all three arsenobenzenes are formed early in the reduction through combination of the free arseno-radicles * PhAs<, which probably exist to a minute amount in the solution in presence of the powerful reducing agent, but the mixed arsenobenzene, being the least soluble, final product of combination of these radicles, is removed from the sphere of action, and is continually formed at the expense of the other arseno-derivatives or radicles, again by means of the minute true solubility of these in the solvent.

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* Fargher's interpretation (T., 1920, **117**, 867) of how a mixed arsenobenzene is formed at all seems unnecessarily complicated; the major difficulty, as to why it is formed exclusively, is left unexplained.

I am indebted to my colleagues, Dr. J. H. Burn, Miss F. M. Durham, and Miss J. Marchal for a comparison of the relative efficacy of some of the arsenobenzenes described in this communication, with a pure sulphur-free salvarsan prepared by hypophosphorous acid. The maximum tolerated and the minimum lethal dose were determined by intravenous injection into mice, and the minimum curative dose by intravenous injection into mice infected with *Trypanosoma equiperdum.* The results obtained are tabulated below and are expressed in milligrams per gram of mouse.

	Dosis Letalis.	Dosis Tolerata.	Dosis Curativa.	C/T.
Disulphino-derivative (IV.)	0·1	0·09	>0·06	—
Disulpho-derivative (VII.)	0·07	0·06	>0·05	—
Monosulphino-derivative * (V.)	0·1	0·09	0·02	1/4·5
Salvarsan (hypophosphorous)	0·2	0·175	0·013	1/13·5

* Base.

A reduction of the basic property of the salvarsan molecule by the introduction of a sulphinic or sulphonic acid group has a dystherapeutic effect, the effect on the toxicity of the sulphonic acid group being somewhat greater than that of the sulphinic. The effect is not, however, so marked as that of the carboxyl group in 5 : 5′-diamino-4 : 4′-dihydroxyarsenobenzene-2 : 2′-dicarboxylic acid (Karrer, *Ber.*, 1915, **48**, 1058), which has a toxic dose of 0·03 mg. per gram of mouse.

The evidence, so far as it goes, shows that the presence of the monosulphinoarsenobenzene in commercial salvarsan does not contribute to the efficacy of this preparation.

EXPERIMENTAL.

Reduction of 3-*Nitro*-4-*hydroxyphenylarsinic Acid with Sodium Hyposulphite: Isolation of* 3-*Amino*-4-*hydroxy*-5-*sulphinophenylarsinic Acid, and* 3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5 : 5′-*disulphinoarsenobenzene.*

3-Nitro-4-hydroxyphenylarsinic acid (106 grams) was dissolved in 800 c.c. of *N*-sodium hydroxide solution in a thin-walled vessel and the solution was mechanically stirred and cooled to —2°. A preliminary experiment on a small-scale batch having determined the minimum quantity of sodium hyposulphite required to decolorise the nitrohydroxy-acid, the calculated quantity was added in four equal portions. For a good commercial sample of sodium hyposulphite 216 grams were required. The temperature before each addition of hyposulphite was lowered to −2°, the successive additions of hyposulphite generally raising the temperature to between 5° and 10°, depending on the efficiency of the stirring and cooling arrangements. On continuing the stirring for an hour or more after the last addition of hyposulphite, 3-amino-4-hydroxyphenylarsinic acid separated in quantity, and to complete the separation the solution was kept in the ice-chamber overnight. The crystals were collected and amounted when dry to 48 grams.

The filtrate was made slightly acid to Congo-paper by the addition of 120 c.c. of concentrated hydrochloric acid and kept at 0° or below for about a week, when a mixture of three substances separated, sodium sulphate, 3-amino-4-hydroxy-5-sulphinophenylarsinic acid, and its corresponding arseno-derivative. These were separated as follows. The solids were collected by filtration, suspended in 100 c.c. of water and warmed with stirring to 40°, when all the sodium sulphate dissolved. The undissolved solids, when collected and dried, amounted to 13·6 grams. A perfect separation of the two components of this mixture was effected by suspending in 80 c.c. of water, and adding 2*N*-ammonia (25 c.c.) until all passed into solution. On addition of 10 c.c. of 4 per cent. calcium chloride solution and thorough mixing, the calcium salt of the arseno-acid was quantitatively precipitated as a gelatinous, yellow mass, which carried down with it a certain amount of the soluble calcium salt of the arsinic acid. The solution was centrifuged and the slightly tinted, water-bright, supernatant fluid syphoned off and acidified to Congo-paper with hydrochloric acid, when pure 3-amino-4-hydroxy-5-sulphinophenylarsinic acid separated. The gelatinous calcium coagulum was resuspended in recently boiled water, well stirred, and again centrifuged. The supernatant fluid, on separation and acidification, gave a second crop of the pure acid. The treatment was repeated so long as any acid separated on acidification, usually three extractions being required in all. The crops of acid were combined and, when air-dried, amounted to 9·3 grams. The gelatinous calcium salt of the arseno-benzene was suspended in air-free water and acidified with hydrochloric acid. The gelatinous acid was obtained by centrifuging and resuspending in fresh water so long as there was any chloride left in the supernatant fluid. When all precipitating ions are removed, the free acid tends to pass into colloidal solution. The gelatinous solid was dried in a vacuum over sulphuric acid and amounted to 2·75 grams.

3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5 : 5′-*disulphinoarsenobenzene*, prepared in this way, is obtained in dark brown, brittle masses still retaining several units per cent. of water, which is almost completely removed by powdering and further drying. The finely ground product is a fawn-coloured substance insoluble in acids, but readily soluble in strong or weak alkalis (Found : N=5·7 *; S=11·9; As=29·6.† $C_{12}H_{12}O_6N_2S_2As_2$ requires N=5·7; S=13·0; As=30·3 per cent.). The somewhat low sulphur content which was consistently observed in several preparations is probably due to the presence of the mixed arseno-derivative. In its properties it agrees substantially with the synthetic product prepared by the reduction of the pure 3-amino-4-hydroxy-5-sulphinophenylarsinic acid.

Properties of 3-*Amino*-4-*hydroxy*-5-*sulphinophenylarsinic Acid* (III).—This acid is almost insoluble in water and crystallises on acidification of solutions of its salts in minute, elongated plates with pointed ends. It remains white and apparently unchanged at 280°. It is insoluble in acids, but dissolves with the production of a bright yellow colour on addition of sodium nitrite, and then couples with alkaline β-naphthol with the production of a deep reddish-brown, soluble dye. The sulphur is not removed by heating with alkaline lead acetate solution, and the acid is remarkably stable to boiling dilute sodium hydroxide solution. The acid, when dissolved in dilute ammonia, gives no precipitate with lithium chloride, calcium chloride, or magnesia mixture in cold or hot solution, but gives an immediate heavy precipitate of sphærocrystals on addition of barium chloride solution at room temperature. Under comparable conditions, the parent acid, 3-amino-4-hydroxyphenylarsinic acid, shows an identical behaviour to nitrous acid and alkaline β-naphthol, gives, however, a beautifully crystalline lithium salt in boiling ammoniacal solution, a crystalline calcium salt under the same conditions, and a microcrystalline magnesium salt. With barium chloride there is slight precipitation. Both acids reduce ammoniacal silver nitrate solution in the cold instantaneously to metallic silver, but only the sulphinic acid decolorises iodine solution, two atoms being consumed. Thus, 0·2971 gram of the dried acid decolorised 20·25 c.c. of *N*/10-iodine, whereas 20 c.c. are required by theory (Found : loss in a vacuum= 2·5, 2·2. $C_6H_8O_6NSAs,\frac{1}{2}H_2O$ requires H_2O=2·9. Found: in dried material, N=4·7; As=25·2; S=10·9. $C_6H_8O_6NSAs$ requires N=4·7; As=25·2; S=10·7 per cent.).

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* All nitrogen estimations were made by the Kjeldahl-Gunning process.

† All arsenic estimations were made by Lehmann's method except where otherwise stated.

Oxidation of 3-Amino-4-hydroxy-5-sulphinophenylarsinic Acid to 3-Amino-4-hydroxy-5-sulphophenylarsinic Acid (VI).

The choice of suitable oxidising agents is limited owing to the reactive *o*-aminophenol group, thus permanganate and sodium *N*-chloro-*p*-toluenesulphonamide proved inapplicable. The calculated amount of iodine oxidises the sulphino-acid quantitatively to the sulpho-acid, but the product is difficult to isolate completely. By use, however, of the calculated amount of 3 per cent. hydrogen peroxide solution, the reaction proceeds quantitatively.

Ten grams of the sulphinic acid were treated with 36 c.c. of 3 per cent. hydrogen peroxide solution. The temperature of the suspension was raised to 40°, when the oxidation proceeded rapidly and exothermally, the temperature rising to 78° with dissolution of the sulphinic acid as the readily soluble sulphonic acid, which crystallised out on keeping in large, well-formed crystals. The yield was almost quantitative.

3-Amino-4-hydroxy-5-sulphophenylarsinic acid differs from the sulphinic acid and the parent 3-amino-4-hydroxyphenylarsinic acid in many respects. The reactions of the latter acids, for comparison, are given above. The sulphonic acid decomposes at 258° (corr.). It is soluble in four times its weight of boiling water. With nitrous acid it gives a deep yellow colour and couples with alkaline β-naphthol with production of a deep reddish-brown, soluble dye. It reduces ammoniacal silver nitrate solution instantaneously. Its ammoniacal solution, on heating, gives a crystalline calcium salt on addition of calcium chloride, and a white precipitate with magnesia mixture. The reaction with barium chloride is characteristic. Addition of the reagent in excess precipitates an oil which dissolves on heating, and on boiling gently a barium salt separates in rosettes of crystals. With lithium chloride there is no precipitation. On boiling the acid with baryta solution, there is no separation of barium sulphate, but, instead, a crystalline barium salt is deposited (Found: $N=4\cdot5$; $S=10\cdot2$; $As=23\cdot5$. $C_6H_8O_7NSAs$ requires $N=4\cdot5$; $S=10\cdot2$; $As=23\cdot9$ per cent.).

3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5 : 5′-*disulphinoarsenobenzene* (IV).

(*a*) *Reduction with Sodium Hyposulphite.*—Two grams of 3-amino-4-hydroxy-5-sulphinophenylarsinic acid, dissolved in 40 c.c. of water containing 6 c.c. of 2*N*-sodium hydroxide, were reduced at 50° for forty-five minutes, by addition of 12 grams of sodium hyposulphite and 3 grams of magnesium chloride. The insoluble arsenobenzene was collected by centrifuging, suspended in recently boiled water, and again centrifuged. The solid was dissolved in 2·7 c.c. of 2*N*-ammonia and centrifuged to remove insoluble impurities. The liquor was acidified to Congo-paper with hydrochloric acid, diluted, and the solid collected by centrifuging. It was resuspended in air-free water and again centrifuged several times until most of the hydrochloric acid had been removed. When dried in a vacuum, it amounted to 1·05 grams (Found: N=5·4; S=13·7; As=27·9. $C_{12}H_{12}O_6N_2S_2As_2$ requires N=5·7; S=13·0; As=30·3 per cent.). It was not found possible to obtain a purer substance by the use of sodium hyposulphite. At 60°, a temperature often reached during the commercial preparation of salvarsan, there is in the present instance fission of some arsenic from the nucleus and a deepening of the colour of the product, the atomic ratios found being N : S : As=1 : 1·56 : 1·36. In this connexion, the author has observed that boiling 3-nitro-4-hydroxyphenylarsinic acid with a concentrated solution of sodium hydrogen sulphite gives *o*-nitrophenol in excellent yield. The extension of this reaction may prove of service in determining the constitution of phenylarsinic acids.

(*b*) *Reduction with Hypophosphorous Acid.*—One gram of the sulphinic acid, suspended in a mixture of 5 c.c. of water and 5 c.c. of glacial acetic acid, was reduced with 5 c.c. of hypophosphorous acid (D 1·14) at 100° (at 60° or 80° only a partial reduction takes place) for one hour. The addition of 0·05 gram of potassium iodide is advantageous. The insoluble, primrose-yellow arsenobenzene was collected by centrifuging, suspended in air-free water, and again centrifuged three or four times until the supernatant liquor was no longer acid to Congo-paper. The product was dried in a vacuum, and the yield was quantitative (Found: N=5·6; S=12·7; As=30·2 per cent.). The qualitative reactions are indistinguishable from those of the corresponding disulphoarsenobenzene described below.

3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5-*sulphinoarsenobenzene Hydrochloride* (V).

(*a*) *Reduction with Sodium Hyposulphite.*—An equimolecular proportion of 3-amino-4-hydroxy-5-sulphinophenylarsinic acid and 3-amino-4-hydroxyphenylarsinic acid, when reduced with this reagent at 50—55° in the usual manner, gave the mixed arsenobenzene. The product and yield are not, however, satisfactory (Found: N=6·1; Cl=8·5; S=6·8; As=32·1. $C_{12}H_{12}O_4N_2SAs_2,HCl$ requires N=6·0; Cl=7·6; S=6·9; As=32·1 per cent.).

(*b*) *Reduction with Hypophosphorous Acid.*—0·88 Gram of 3-amino-

4-hydroxyphenylarsinic acid and 1·12 grams of its 5-sulphino-derivative were reduced in a solution made up from 10 c.c. of hypophosphorous acid (D 1·14), 5 c.c. of glacial acetic acid, 5 c.c. of water, and a crystal of potassium iodide, at 100° for one hour. The insoluble yellow solid was collected by centrifuging, suspended in recently boiled water, and again centrifuged, then treated twice with excess of 2*N*-hydrochloric acid and centrifuged each time. Finally, the hydrochloride was suspended twice in air-free water, centrifuged, and dried in a vacuum. The yield of the initial base was quantitative, the yield of the hydrochloride was smaller (1 gram), owing to losses in washing (Found: N=6·0; Cl=7·7; S=6·9; As=31·7 per cent.). The qualitative reactions are indistinguishable from those of the corresponding monosulpho-derivative described below.

3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5 : 5′-*disulphoarsenobenzene* (VII).

Reduction with Hypophosphorous Acid.—One gram of 3-amino-4-hydroxy-5-sulphophenylarsinic acid was suspended in 5 c.c. of water, 5 c.c. of glacial acetic acid, and 5 c.c. of hypophosphorous acid (D 1·14). A crystal of potassium iodide was added and the temperature raised to 55°. On stirring, the sulphonic acid dissolved and reduction to the arsenobenzene was rapid. After one hour, the arsenobenzene was collected by centrifuging, suspended in recently boiled water, and centrifuged four times. The final supernatant liquor was barely acid to litmus. The yield was quantitative (Found: N=5·4; S=12·6; As=28·5. $C_{12}H_{12}O_8N_2S_2As_2$ requires N=5·3; S=12·2; As=28·5 per cent.).

3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5 : 5′-*disulphoarsenobenzene* is insoluble in water and does not form salts with acids. It diazotises, forming a deep yellow solution and couples then with β-naphthol. It is soluble in 2*N*-sodium hydroxide solution, but is precipitated by a slight excess. Its solution in sodium carbonate is precipitated by excess of concentrated sodium carbonate solution, and likewise its solution in dilute ammonia by concentrated ammonia solution. This precipitation is apparently a coagulating or flocculating property of the hydroxyl ion. The compound dissolves readily in sodium hydrogen carbonate solution and is not precipitable by a saturated solution of this reagent. It is not appreciably soluble in saturated sodium acetate solution, but dissolves on dilution. The ammoniacal solution gives an immediate and copious gelatinous precipitate with calcium and barium chlorides, with magnesia mixture, and with lanthanum or thorium nitrate. With lithium chloride the precipitate is slight.

Hydrolysis of 3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5 : 5′-*disulphoarsenobenzene.*—One gram of the sulphoarsinic acid was reduced as described above to the arsenobenzene. The still damp solid was dissolved in 20 c.c. of hot water by addition of 2 c.c. of saturated sodium acetate solution and heated in a sealed tube for ten hours at 100°. The red solution was made acid to Congo-paper with hydrochloric acid and filtered. The colourless filtrate was extracted with ether, which only removed acetic acid. The aqueous solution was reduced by saturation with sulphur dioxide, the excess removed from the warmed solution in a vacuum, and the arsenic completely removed as arsenious sulphide by passing hydrogen sulphide. The filtered solution on concentration gave 0·3 gram of pure 6-*aminophenol*-o-*sulphonic acid*, crystallising in long, silky needles (Found: in air-dried solid, $H_2O=4{\cdot}2$; in anhydrous material, $N=7{\cdot}5$. $C_6H_7O_4NS,\frac{1}{2}H_2O$ requires $H_2O=4{\cdot}5$; $C_6H_7O_4NS$ requires $N=7{\cdot}4$ per cent.). It differs from 6-aminophenol-*m*-sulphonic acid, with which a direct comparison was made, in forming a very sparingly soluble barium salt, in its slighter stability in alkaline solution, in forming a hydrate, and in not forming a sparingly soluble diazo-oxide.

3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5-*sulphoarsenobenzene Hydrochloride.*

Reduction with Hypophosphorous Acid.—1·15 Grams of 3-amino-4-hydroxy-5-sulphophenylarsinic acid and 0·85 gram of 3-amino-4-hydroxyphenylarsinic acid were reduced with a mixture of 10 c.c. of hypophosphorous acid (D 1·14), 5 c.c. of water, and 5 c.c. of glacial acetic acid at 60°. A crystal of potassium iodide was added as a catalyst. Both acids dissolved at this temperature and the quantitative separation of the mixed arsenobenzene was complete at the end of one hour. The working up of the product as hydrochloride for analysis was exactly as described above for the corresponding mixed sulphino-derivative. The yield was 1·8 grams (Found: $N=5{\cdot}7$; $Cl=7{\cdot}1$; $S=6{\cdot}9$; $As=30{\cdot}8$.* $C_{12}H_{12}O_5N_2SAs_2,HCl$ requires $N=5{\cdot}8$; $Cl=7{\cdot}3$; $S=6{\cdot}6$; $As=31{\cdot}1$ per cent.).

3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5-*sulphoarsenobenzene hydrochloride* is sparingly or slowly soluble in water. It is soluble in 2*N*-sodium hydroxide solution and is precipitated by excess. It is, however, soluble in dilute or concentrated ammonia. It only dissolves slowly in sodium carbonate solution and is not precipitated by excess of the saturated solution. It is insoluble in sodium hydrogen carbonate solution. The ammoniacal solution forms gelatinous

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* Estimated gravimetrically by the Carius method as $Mg_2As_2O_7$. Lehmann's method gave low results.

precipitates with calcium, barium, or magnesium chloride, but with lithium chloride only on adding excess.

3 : 3′-*Diamino*-4 : 4′-*dihydroxy*-5-*sulpho*-5′-*sulphinoarsenobenzene*.

Reduction of an equimolecular mixture of the sulpho- and sulphinoarsinic acids with hypophosphorous acid at 100° proceeded normally. The yield was quantitative. The product is indistinguishable in its qualitative reactions from either the disulphoarsenobenzene or the disulphinoarsenobenzene (Found : N=5·4; S=12·1; As=29·5. $C_{12}H_{12}O_7N_2S_2As_2$ requires N=5·5; S=12·6; As=29·4 per cent.).

The Constituents of Salvarsan insoluble in Methyl Alcohol.

9·5 Grams of a commercial salvarsan *A* containing 2·7 per cent. of sulphur were dissolved in 29 c.c. of dry methyl alcohol (compare Fargher and Pyman, *loc. cit.*) and kept overnight in absence of air and moisture. The solidified contents were broken up and centrifuged in stoppered tubes, the supernatant liquor syphoned off, and the yellow solid mixed with 30 c.c. of dry methyl alcohol. The contents were again centrifuged and submitted to fresh quantities of methyl alcohol five times in all. The final product was dried in a vacuum and then weighed 2·3 grams or 24 per cent. of the weight of the starting material. The finely powdered solid had a bright yellow colour (Found: N=5·3; Cl=7·25; S=5·7. A second preparation from the same original batch of material gave N=5·3; Cl=7·4; S=5·8; As=30·0 *; whence the ratio of the atoms is N : As : S : Cl=2 : 2·1 : 0·94 : 1·1. Fargher and Pyman, for the small quantity of material isolated by them, found Cl=6·8; S=5·1; As=30·8. The mixed sulphinoarsenobenzene hydrochloride, $C_{12}H_{12}O_4N_2SAs_2$,HCl, requires N=6·0; Cl=7·6; S=6·9; As=32·1 per cent., whilst the mixed sulphoarsenobenzene hydrochloride, $C_{12}H_{12}O_5N_2SAs_2$,HCl, requires N=5·8; Cl=7·3; S=6·6; As=31·1 per cent.). The approximate agreement with these monohydrochlorides is fortuitous, for the product contained a portion of its sulphur in the form of sulphate. Examination of several samples of the constituent insoluble in methyl alcohol from other batches of commercial salvarsan showed that in general this insoluble constituent is a mixture, and consists of 3 : 3′-diamino-4 : 4′-dihydroxy-5-sulphinoarsenobenzene monohydrochloride (the possibility of the presence of the corresponding sulpho-derivative is not excluded, since there is no means of detecting one in the presence of the other, the iodine absorption figures proving valueless) and

* By Carius as $Mg_2As_2O_7$.

"salvarsan sulphate" and "hydrochloride." The latter are probably chiefly present as the mixed salts analogous to the well-known mixed salts of dibasic quinine, such as $2Q,H_2SO_4,2HBr$. There is no evidence of the presence of a monosulphamic acid, as suggested by Fargher and Pyman. These statements are supported by the following evidence.

Twenty-one grams made up from thirty-five samples, each 0·6 gram, of successive batches of a well-known make of salvarsan, were dissolved or suspended in 63 c.c. of dry methyl alcohol for twenty-four hours and then worked up for the insoluble constituent exactly as described above. There were obtained 1·8 grams of dry solid, which on analysis gave N=5·6; total S=3·3; S as sulphate=1·9; Cl=8·4; As=31·5 per cent., whence the atomic ratios are

N.	As.	Cl.	Total S.	Free S as SO_4.	Combined S.
2	2·09	1·18	0·51	0·29	0·22

On the assumption that the constituents are as stated above, it is evident that out of 200 NH_2-groups 118 are combined with hydrochloric acid, 58 with sulphuric acid, and 22 neutralised internally by the sulphinic acid group, that is to say, the acid groups present are equivalent within 1 per cent. to the NH_2-groups.

Reactions of the Substance insoluble in Methyl Alcohol.—It dissolves in water completely, first passing through a gelatinous state. On addition of neutral barium chloride solution there is immediate separation of barium sulphate, and, after centrifuging, the clear supernatant liquor gives no further separation of barium sulphate on heating, either alone or with acids or alkalis. This proves the absence of the sulphamo-group, $\cdot NH\cdot SO_3H$ (Traube, *Ber.*, 1890, **23**, 1653). The presence of "salvarsan sulphate" in a soluble state is at first surprising, as the pure substance is insoluble in cold water. Experiment has, however, shown that a preparation of the pure sulphate dissolves readily on the addition of dilute hydrochloric acid or sodium chloride solution and is readily soluble up to 33 per cent. in "salvarsan hydrochloride" solution.

When dissolved in thirty parts of water and treated with 3*N*-hydrochloric acid, a flocculent precipitate was obtained. On collecting this by centrifuging and washing in the centrifuge, first with *N*-hydrochloric acid and then with water, and drying the product, a substance was obtained which contained S= 5·7; N=5·9 per cent. There was no free sulphate present. This evidently consists of the mixed arseno-derivative, 3 : 3′-diamino-4 : 4′-dihydroxy-5-sulphinoarsenobenzene hydrochloride, in a crude state. Unlike the starting material, it was no longer soluble or only very slowly so in water, in this respect showing a close resemblance to the synthetic product.

Oxidation of the Constituent insoluble in Methyl Alcohol.—2·35 Grams of the insoluble constituent from salvarsan *A* were oxidised in alkaline solution by hydrogen peroxide, following Ehrlich and Bertheim's process for salvarsan (*Ber.*, 1912, **45**, 756). By acidifying to Congo-paper with hydrochloric acid and concentrating, 0·8 gram of 3-amino-4-hydroxyphenylarsinic acid was obtained. The mother-liquors were evaporated to dryness after neutralising with sodium carbonate, the residue was dissolved in a small volume of water, the solution filtered from a small quantity of insoluble material, then made alkaline with ammonia, and treated with barium chloride solution. On heating on the water-bath, a pigmented crystalline barium salt separated, which on acidification gave eventually 0·1 gram of pure 3-amino-4-hydroxy-5-sulphophenylarsinic acid. Its identity was proved by comparison with the pure material obtained by oxidation of the sulphinic acid. Both melted at the same temperature and showed an identical behaviour in the calcium salt, and also when diazotised and coupled, and in other reactions.

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CXXII.—*The Sorption of Hydrogen by Amorphous Palladium.*

By JAMES BRIERLEY FIRTH.

IN a previous communication (T., 1920, **117**, 171) the author showed that in the case of palladium foil the sorption of hydrogen is essentially "adsorption" below 0° and, further, that "absorption" diminishes with lowering of temperature below 0°, whereas adsorption increases.

Mond, Ramsey, and Shields (*Phil. Trans.*, 1898, [*A*], **191**, 105) found that at 0° palladium black sorbed about 853 volumes of hydrogen. Hemptinne (*Bull. Acad. roy. Belg.*, 1898, [iii], **36**, 155) finds that, when palladium is cooled to −78° and then exposed to hydrogen, the volume of gas sorbed is much smaller than at 20°.

Paal and Amberger (*Ber.*, 1905, **38**, 1394) found that the sorption of hydrogen by palladium black was considerably increased when the palladium was heated in hydrogen at 110° and then cooled to $-10°$.

Gutbier, Gebhardt, and Ottenstein (*Ber.*, 1913, **46**, 1453), by a similar method, showed that the sorption diminished from 100° to 20° and then increased from 20° to $-50°$.

Sieverts (*Zeitsch. physikal. Chem.*, 1914, **88**, 105) studied the sorptive capacity of the various forms of palladium and showed that from 100° to 1500° sorption diminishes with rise of temperature. At higher temperatures, amorphous palladium and crystalline palladium sorb hydrogen by solution merely; at lower temperatures, amorphous palladium takes up further quantities by adsorption.

EXPERIMENTAL.

The object of the experiments described in the present communication was to determine the sorption capacity of palladium black at temperatures ranging from 100° to about $-190°$ (liquid-air temperature) by two distinct methods:

(*a*) The palladium was heated at 100° and the hydrogen then admitted. The palladium remained in contact with the hydrogen at 100° for twenty minutes and was then cooled slowly in hydrogen to the required temperature and an equilibrium established at atmospheric pressure.

(*b*) The palladium was cooled to the required temperature in a vacuum and hydrogen then slowly admitted until an equilibrium was established at atmospheric pressure.

The results obtained by these methods are subsequently referred to as series (*a*) and (*b*) respectively.

All experiments were carried out in duplicate. Prior to exposure to hydrogen, the palladium, as prepared, was in every case heated at 110° and a vacuum maintained for twenty-four hours, the palladium being open to a tube containing phosphoric oxide in order to remove as much water as possible.

The former method is similar to that of Paal and Amberger, and the latter to that of Hemptinne. The results of these observers have been looked upon as contradictory, but the author hopes to be able to show that it is possible for both to be correct, the difference in the results being due to the methods employed.

The apparatus used was the same as that already described (T., 1920, **117**, 171).

The first problem was to obtain a good quality of palladium black.

It has previously been shown that the sorption of hydrogen by palladium is determined by the two forms of the metal, the amorphous and the crystalline. Further, the amorphous form is the more active and tends to pass into the crystalline variety.

Palladium black was obtained by four different methods: by the reduction of palladous chloride, (i) by heating in a current of hydrogen, (ii) with hydrazine sulphate, (iii) with a weak solution of sodium formate, and (iv) by the reduction of the oxide in a current of hydrogen. The sorptive capacity of each specimen was determined at 0° by methods (*a*) and (*b*) respectively. The results were as follows:

	(i)	(ii)	(iii)	(iv)
(*a*)	796 vols.	801 vols.	879 vols.	852 vols.
(*b*)	702 ,,	736 ,,	847 ,,	804 ,,

The palladium black invariably contained oxygen, hence the volume of hydrogen admitted was always greater than that evolved on heating to a dull red heat, the difference between the two quantities being a measure of the amount required to convert the oxygen to water. The volumes in all cases are corrected to 0° and 760 mm.

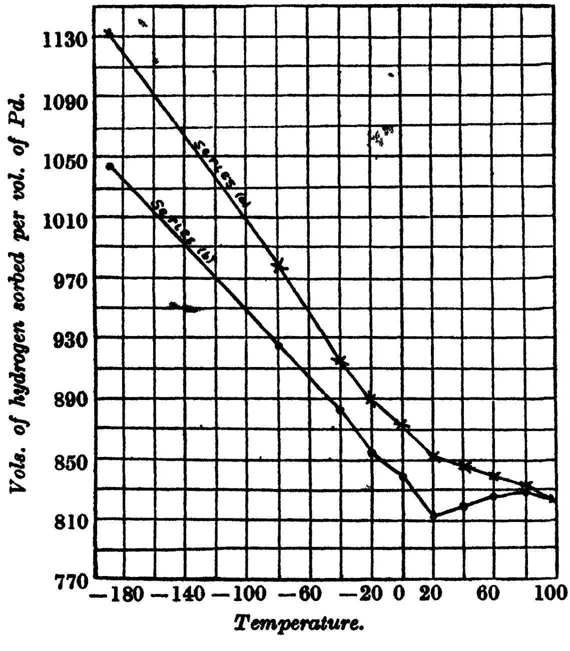
It will be observed that there is a difference in the activity of the various specimens, particularly in series (*b*). The explanation for this difference in the activity lies in the non-homogeneity of the palladium black. The two phases, crystalline and amorphous, are present in all specimens, but in different proportions, and as the activity of the amorphous variety is greater than that of the crystalline, the highest value represents the purest form of amorphous palladium. Again, the difference between series (*a*) and (*b*) is greatest in sample (i) and least in (iii). In series (*a*), both the amorphous and the crystalline varieties would be saturated with hydrogen, whereas in series (*b*) the sorption would be principally by the amorphous form.

The above experiments show that the most satisfactory palladium black is obtained by reducing a solution of the chloride with a weak solution of sodium formate. This method was employed to prepare the palladium black used in the following experiments, and the exact details of the preparation are as given by Mond, Ramsey, and Shields (*loc. cit.*).

The volume of hydrogen sorbed was determined by heating the palladium black to a dull red heat and measuring the volume of the hydrogen pumped off. At the high temperature necessary to expel the whole of the hydrogen, the palladium black was converted into palladium sponge, and the ratio between the amorphous and the crystalline varieties would probably be changed. For this reason it was necessary to use a fresh sample of palladium black for each experiment. An average of four analyses of the palladium black used was :— Pd=89·1; PdO=10·1; H_2O=0·8 per cent.

The sorptive capacity of palladium black was determined at temperatures ranging from 100° to the temperature of liquid air (about −190°). The temperatures between 0° and liquid-air temperature were obtained by adding solid carbon dioxide to alcohol in the required proportions, the temperature being kept constant by adding small quantities of solid carbon dioxide from time to time.

FIG. 1.



Except where expressly stated to the contrary, the palladium was not subjected to a temperature of more than 110° prior to being used, neither did it receive any preliminary treatment with hydrogen.

Two distinct series of experiments were carried out according to methods (*a*) and (*b*) respectively.

The hydrogen was sorbed very rapidly, only a very small amount being taken up after the first few minutes. The equilibrium was established more rapidly at the lower temperatures and below 0° was almost instantaneous.

The results are given in the following table and are shown graphically in Fig. 1.

Series (*a*). Temperature.	Series (*a*). Vols. of hydrogen sorbed per vol. of Pd.	Series (*b*). Temperature.	Series (*b*). Vols. of hydrogen sorbed per vol. of Pd.
100°	823	100°	823
80	832	80	828
60	838	60	825
40	846	40	818
20	851	20	811
0	872	0	839
−20	888	−20	853
−40	914	−40	882
−79	976	−80	926
−190	1132	−190	1044

The volumes of hydrogen are corrected to N.T.P. and the weight of palladium is corrected for oxygen and water from an average analysis. The density of palladium black was taken as 11·9.

It will be observed from the results of the two series that there is a persistent difference, which becomes more pronounced below 0°. This is due to the presence of crystalline palladium in the black. It has previously been shown (*loc. cit.*) that the sorptive capacity of crystalline palladium is considerably diminished at temperatures below 0°. Now, in series (*a*), the crystalline palladium would take up an appreciable amount of hydrogen prior to being cooled, this hydrogen being retained, whereas in series (*b*) the amount of hydrogen sorbed by the crystalline variety would be very small, being almost nil at the lower temperatures; hence the difference between the two series.

It would appear, therefore, that the purer the palladium black used, the more nearly will the two sets of results coincide, and, conversely, the greater the proportion of crystalline palladium, the greater the difference between the two series. Further, a palladium black containing a moderate proportion of the crystalline variety would have a much smaller sorptive capacity at low temperatures than at temperatures between 0° and 100°. This would explain the difference between the conclusions of Paal and Amberger on the one hand and Hemptinne on the other. In the first case, the palladium was heated in hydrogen at 110° and cooled in hydrogen to the required temperature, hence both the crystalline and the amorphous form would be active; whereas Hemptinne cooled the palladium to −78° before admitting hydrogen, thus eliminating to a large extent that portion of the palladium which was crystalline, and since he obtained a considerable diminution in the volume sorbed, as compared with the volume at 20°, his palladium must have contained a moderate proportion of the crystalline palladium. This view is further supported by the fact that he observed a sudden increase in the volume of hydrogen sorbed on allowing the temperature to rise to 20°, at which temperature the crystalline variety would begin to sorb hydrogen rapidly, particularly in contact with highly charged amorphous palladium.

In order further to test this view, the following experiments were carried out:

(1) The palladium black was saturated with hydrogen at 100° and the hydrogen then expelled at a red heat. The black was thereby converted into palladium sponge, the colour changing from black to pale grey. It was then heated at a dull red heat in a vacuum for three hours. The sample was then divided into two parts and the sorptive capacity determined at $-20°$ as before, with the result:

(*a*) 851 vols. (*b*) 796 vols.

(2) The palladium from (1) was heated at a dull red heat for a further period of six hours and the sorptive capacity again determined at $-20°$ under the two conditions, with the following results:

(*a*) 813 vols. (*b*) 744 vols.

It would appear, therefore, that the effect of heating has been to increase the amount of the crystalline palladium, thereby increasing the difference between the two sets of results.

The absence of absorption by the crystalline variety at low temperatures may be apparent rather than real. It is quite possible that the rate of diffusion is so slow at low temperatures that within the duration of the experiments absorption is not an appreciable factor.

On again comparing the results of the two series, it will be observed that in series (*a*) the volumes sorbed increase continuously from 100° to $-190°$, the rate of increase being greater below 20°; whereas in series (*b*) the volumes diminish slightly from 100° to 20° and then increase from 20° to $-190°$. Hence it would appear that there is a minimum sorption at 20°. The minimum obtained by Gutbier, Gebhardt, and Ottenstein gave a decrease of 93 volumes over the range 100° to 20°. The maximum diminution obtained by the author over the same range was 11 volumes.

Summary.

(1) The sorptive capacity of palladium black varies according to the method of preparation.

(2) Palladium black contains both amorphous and crystalline palladium, the proportion of each varying with the conditions under which it was originally prepared.

(3) The sorptive capacity of palladium black at low temperatures depends on the temperature at which sorption begins.

(4) Palladium black saturated with hydrogen at 100° sorbs further quantities of hydrogen when gradually cooled in the gas.

(5) A comparison of the sorptive capacity at definite temperatures varying from 100° to −190° shows a slight decrease from 100° to 20° and a continuous increase from 20° to −190°.

(6) When palladium black is heated, the proportion of the crystalline variety increases.

THE CHEMICAL DEPARTMENT,
UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, May 10th*, 1921.]

CXXIII.—*The Sorption of Alcohol and Water by Animal Charcoal.*

By JOHN DRIVER and JAMES BRIERLEY FIRTH.

A CONSIDERABLE amount of data has already been published regarding the sorption of substances in solution by charcoal. In calculating the results, in nearly every case it has been assumed that the solvent is not sorbed, or the amount sorbed is so small that it can be neglected.

One of us has already shown (Firth, *Trans. Faraday Soc.*, 1921, **16**, 434) that in the case of the sorption of iodine from solution in organic solvents the nature of the solvent materially affects the rate of sorption, and also that the final equilibrium (which is only attained after a very long period) is to some extent dependent on the solvent. One factor that influenced the sorption was the solubility of the dissolved substance in the liquid solvent.

The sorption of liquids does not appear to have been studied to any great extent and the quantitative data available are comparatively small.

Gurvitsch (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 805) has made a study of the sorption of water and various organic liquids by fuller's earth, bone charcoal, and kaolin, and obtained the following important result—that the volumes of liquid adsorbed vary over a relatively small range from 0·61 to 0·684 c.c. per gram of sorbing substance. He attributes adsorption to physicochemical forces and rejects the view that it is due to purely chemical forces on the following grounds. (1) The amounts of the different liquids adsorbed by a given amount of adsorbent are not in agreement with stoicheiometric relations. (2) The range of action of the forces causing adsorption is always of the order 3×10^{-6} cm., whereas the range of action of the force of chemical affinity is limited to distances of atomic order or, at most, to the distances separating neighbouring molecules. The sphere of action of physicochemical forces is many times greater. (3) The heat of reaction between any two elements is, generally speaking, greater the more dissimilar are the elements. In the action of residual chemical energy (physicochemical force) we see just the reverse: hydrocarbons generate much more heat with charcoal than with fuller's earth or kaolin; alcohols act in the reverse manner.

Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1848), in a criticism of the work of Gurvitsch, rejects the view that sorption is due to physicochemical forces, and states " the forces involved in adsorption are strictly chemical in nature, that is, they do not differ in any essential respect from the forces causing the formation of typical compounds." The absence of stoicheiometric relationship can be taken as proof, not of the absence of chemical combination, but that it is simply the result of steric hindrance. The following quotation gives Langmuir's view of the processes occurring during the adsorption of ethyl alcohol by charcoal. " The hydroxyl groups of the alcohol are attracted to the carbon atoms, so that as many carbon atoms as possible come into contact (or combine) with the hydroxyl groups. The ethyl groups fill up many of the small cavities, and, in other ways, prevent the hydroxyl groups from coming into contact with the carbon atoms. The larger pores or cavities are, however, covered over with a single layer of molecules. When the vapour is saturated, it is evident that these cavities must gradually become filled with liquid. But this is to be classed as capillary phenomena and not as adsorption. It has, for example, nothing to do with the forces acting between the carbon atoms and the hydroxyl groups.

" Under these conditions it is only natural that the volume absorbed should be about the same for different liquids, since it is simply a measure of the total volume of the larger pores."

Bakr and King (this vol., p. 454), in a communication published since this work was completed, show that the sorption of benzene from iodine solutions is less than that from the pure solvent. They further show that the effect of neglecting the sorption of the solvent benzene in calculating the sorption of iodine is very small in this case.

The object of the present communication was to study the sorption of water and alcohol by animal charcoal and also the sorptive effect with mixtures of alcohol and water.

EXPERIMENTAL.

The animal charcoal used was Merck's highly purified variety, and it gave 4·435 per cent. of ash. It was digested several times with concentrated hydrochloric acid, washed with water, and finally boiled with distilled water until free from phosphates and chlorides; the ash was then 1·05 per cent. and the density 1·966. The charcoal was very finely powdered. The alcohol was dried for several days over calcium oxide and distilled, then dried with metallic calcium and again distilled, the first and the last portions being rejected. Its density at 25° was 0·78572.

Ordinary distilled water was treated with alkaline potassium permanganate and distilled, the middle portion only being used. This was then twice redistilled; the product gave no appreciable residue on evaporation.

The Determination of the Sorption of (a) *Water* (b) *Alcohol.*

The charcoal was heated at a dull red heat in a vacuum for about three hours and then allowed to cool in a vacuum. A quantity of the charcoal was then quickly weighed out into a well-stoppered tube fitted with a leading-tube and tap. About 5 c.c. of distilled water were introduced into a similar tube and the two tubes connected by means of a T-piece, also fitted with a tap. The apparatus was exhausted and placed in a thermostat at 25°. The tube containing the charcoal was carefully disconnected at definite intervals and weighed, until the weight became constant.

A similar series of results was obtained, using alcohol instead of water. The results are given in the following table, where m is the weight of charcoal used and x the c.c. of liquid sorbed.

TABLE I.

Water.

$m=1·0398$ grams.

Time. Days.	x	$\frac{x}{m}$
1	0·0118	0·0113
4	0·0210	0·0202
8	0·0298	0·0286
14	0·0408	0·0392
18	0·0480	0·0462
22	0·0553	0·0532
33	0·0732	0·0704
48	0·1094	0·1062
60	0·1394	0·1340
70	0·1398	0·1345
80	0·1397	0·1345

Alcohol.

$m=1·1272$ grams

Time. Days.	x	$\frac{x}{m}$
1	0·1464	0·1299
2	0·2753	0·2442
4	0·3469	0·3077
7	0·4147	0·3679
10	0·4867	0·4318
15	0·5596	0·4965
20	0·5963	0·5299
25	0·6292	0·5582
37	0·6894	0·6205
60	0·6894	0·6205

Sorption of Alcohol from Mixtures of Alcohol and Water.

The change in the composition of the various mixtures of alcohol and water after treatment with charcoal for twenty-four hours was determined by accurately measuring the change in the density.

Mixtures of alcohol and water were carefully prepared and the density determined by the pyknometer method. Twenty-five c.c. of the mixture were measured into a well-stoppered flask of 50 c.c. capacity and two grams of purified animal charcoal, which had previously been heated in a vacuum at a dull red heat for three hours and cooled, were introduced. The flask was then placed in a thermostat at 25°, and repeatedly shaken. After twenty-four hours, the charcoal was filtered off and the density of the mixture redetermined. From this new density the composition of the mixture was obtained. The results are given in Table II.

In calculating the amount of alcohol sorbed it has been assumed that no water has been sorbed during the period under observation. The error introduced is negligible, since the amount of water sorbed is so small that it would not materially affect the result. All densities were determined at 25°.

TABLE II.

Volume percentage of alcohol before sorption.	Density before sorption.	Density after sorption.	Volume percentage of alcohol after sorption.	$\frac{x}{m}$
90	0·82511	0·82678	89·59	0·504
75	0·86906	0·87100	74·26	0·3590
60	0·90581	0·90804	58·95	0·3203
50	0·92715	0·92912	48·99	0·2475
40	0·94565	0·94712	38·84	0·2368
25	0·96756	0·96864	23·74	0·2066
10	0·98482	0·98557	9·31	0·0701
	0·99135	0·99158	4·88	0·0158

Rate of Sorption of Alcohol from Alcohol–Water Mixtures.

The rate of sorption of alcohol was determined by measuring the rate of change of density. A number of flasks were set up as before and the contents examined after different intervals of time. The results are given in Table III for 90, 50, and 5 per cent. mixtures by volume.

Discussion of Results.

The results in Table I show that the rate of sorption of water is exceedingly slow, requiring about seventy days to attain equilibrium; in the case of alcohol, equilibrium is attained in

TABLE III.

90 per cent. Mixture.

Time in hours.	Density.	Volume percentage of alcohol.	
0	0·82511	90	
24	0·82678	89·59	0·504
48	0·82711	89·49	0·554
72	0·82725	89·46	0·641

50 per cent. Mixture.

Time in hours.	Density.	Volume percentage of alcohol.	$\frac{x}{m}$
0	0·92715	50·0	—
19	0·92858	49·20	0·1988
42	0·92979	48·57	0·3475
62	0·93108	47·94	0·4918
90	0·93245	47·28	0·6452
100	0·93426	47·28	0·6452

5 per cent. Mixture.

Time in hours.	Density.*	Volume percentage of alcohol.	$\frac{x}{m}$
0	0·99154	5	—
24	0·99158	4·88	0·0158
48	0·99157		
72	0·99158		

* The change in density for low concentrations was so small that the results were not satisfactory, but the change in concentration was certainly very small in comparison with the results obtained at higher concentrations.

about thirty-seven days. Water is sorbed to the extent of 0·13 c.c. per gram of charcoal, whereas in the case of alcohol the value is nearly five times this amount, namely, 0·62 c.c. This result is not in agreement with that put forward by Gurvitsch, who obtained similar values for both alcohol and water with the same sorbing agent. The value for alcohol falls within the same range as that given by Gurvitsch for fuller's earth as sorbing substance, but this is probably only a coincidence.

The results given in Table II for alcohol–water mixtures show that alcohol is preferentially sorbed throughout, and, further, that the amount of alcohol sorbed in the first twenty-four hours depends on the alcohol content of the mixture. In the case of 90 per cent. alcohol the charcoal has taken up nearly five-sixths of the amount required for saturation. As the water content increases, the amount of alcohol sorbed diminishes, and where the alcohol content is less than 25 per cent. the sorption becomes very small.

From Table III it will be observed that, except for low alcohol concentration, the effect of the water is to reduce the rate of sorption of alcohol, since the charcoal finally becomes saturated with respect to alcohol. When the alcohol content had fallen to about 4·88 per cent., it was not possible to detect with certainty any further change in concentration. Langmuir explains the results of Gurvitsch as being due to a large extent to capillarity. The results here given do not support this view; the values for alcohol and water are widely different, whereas if capillarity was a fundamental phenomenon, the values should be very similar. Capillarity is a factor, without doubt, but when the sorbent is in a very finely divided state, as in the present case, it is not a fundamental factor. In any case it is a variable factor depending to a large extent on the size of the particles of the given sorbent.

Within the limits of the experiments herein described, the sorption of liquids by charcoal is not independent of the nature of the liquid. Steric hindrance, as indicated by Langmuir, varies with different liquids, and, accepting this view, it is to be expected that the volumes of different liquids sorbed by unit weight of sorbent will vary over quite a large range.

In order to test further the conclusions of Gurvitsch, experiments with other liquids have been undertaken.

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CXXIV.—*Action of Magnesium Phenyl Haloids on Diphenylchloroacetyl Chloride. Constitution of Triphenylvinyl Alcohol.*

By ALEX. MCKENZIE and JOHN SCOTT WALKER BOYLE.

THE chlorine atom in α-chloro-α-phenylpropionic acid undergoes substitution by the hydroxyl group with great readiness, even when the acid is shaken with water at the ordinary temperature (McKenzie and Clough, T., 1910, **97**, 1016), whilst the chlorine in diphenylchloroacetic acid is very easily removed by magnesium phenyl bromide (McKenzie, Drew, and Martin, T., 1915, **107**, 26).

It was accordingly anticipated that diphenylchloroacetyl chloride might display abnormality when acted on by Grignard reagents, and the experiments of which a description is now given show that this expectation was borne out.

In the event of triphenylacetyl chloride being produced by the substitution of the phenyl group for chlorine, thus:

$$\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C}{<}\genfrac{}{}{0pt}{}{\mathrm{Cl}}{\mathrm{COCl}}+\mathrm{PhMgBr}\rightarrow\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C}{<}\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{COCl}},$$

the product should be β-benzopinacolin, since Schmidlin (*Ber.*, 1910, **43**, 1137) has shown that the change,

$$\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C}{<}\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{COCl}}+\mathrm{PhMgBr}\rightarrow\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C}{<}\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{COPh}},$$

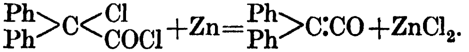
can be effected. On no occasion, however, did we obtain either β-benzopinacolin or pentaphenylethanol when diphenylchloroacetyl chloride was acted on by magnesium phenyl bromide. On the other hand, when the acid chloride was added to an excess of the Grignard reagent, the main product was triphenylvinyl alcohol, a curious result which is to be attributed to a novel application of the Grignard reagent involving the transient existence of a keten. This explanation is by no means improbable when Schmidlin's observation of the formation of triphenylmethyl by the action of magnesium phenyl iodide on triphenylacetyl chloride is recalled:

$$2\mathrm{Ph_3C{\cdot}COCl}+2\mathrm{PhMgI}=2\mathrm{CPh_3}+2\mathrm{CO}+\mathrm{Ph{\cdot}Ph}+2\mathrm{MgClI}.$$

Just as in the case investigated by us, the Grignard reagent here splits off halogen from the acid chloride, behaving in the same way as certain metals; molecular silver, for instance, gives triphenylmethyl with triphenylacetyl chloride,

$$\mathrm{Ph_3C{\cdot}COCl}+\mathrm{Ag}=\mathrm{CPh_3}+\mathrm{CO}+\mathrm{AgCl},$$

whilst Staudinger obtained diphenylketen from zinc and diphenylchloroacetyl chloride, $\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C}{<}\genfrac{}{}{0pt}{}{\mathrm{Cl}}{\mathrm{COCl}}+\mathrm{Zn}=\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C{:}CO}+\mathrm{ZnCl_2}$.



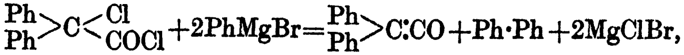
A parallel action on the splitting off of halogen by the Grignard reagent is also quoted by Schmidlin and v. Escher (*Ber.*, 1910, **43**, 1153), who, in attempting to form hexaphenylethane, found that two chlorine atoms are withdrawn from the molecule of *s*-dichlorotetraphenylethane:

$$\mathrm{Ph_2CCl{\cdot}CClPh_2}+2\mathrm{PhMgBr}=\mathrm{Ph_2C{:}CPh_2}+\mathrm{Ph{\cdot}Ph}+2\mathrm{MgClBr}$$

(compare Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2940).

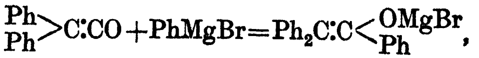
The formation of triphenylvinyl alcohol is probably due to the following changes:

(*a*)



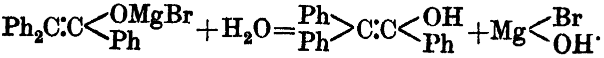
$$\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C}{<}\genfrac{}{}{0pt}{}{\mathrm{Cl}}{\mathrm{COCl}}+2\mathrm{PhMgBr}=\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C{:}CO}+\mathrm{Ph{\cdot}Ph}+2\mathrm{MgClBr},$$

(*b*)



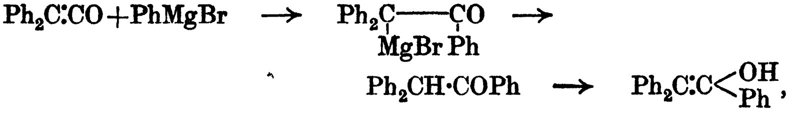
$$\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C{:}CO}+\mathrm{PhMgBr}=\mathrm{Ph_2C{:}C}{<}\genfrac{}{}{0pt}{}{\mathrm{OMgBr}}{\mathrm{Ph}},$$

(*c*)



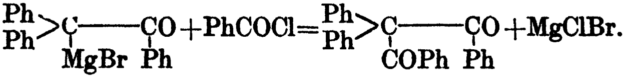
$$\mathrm{Ph_2C{:}C}{<}\genfrac{}{}{0pt}{}{\mathrm{OMgBr}}{\mathrm{Ph}}+\mathrm{H_2O}=\genfrac{}{}{0pt}{}{\mathrm{Ph}}{\mathrm{Ph}}{>}\mathrm{C{:}C}{<}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{Ph}}+\mathrm{Mg}{<}\genfrac{}{}{0pt}{}{\mathrm{Br}}{\mathrm{OH}}.$$

Assuming the intermediate production of diphenylketen, the formation of triphenylvinyl alcohol is readily understood, since Staudinger (*Annalen*, 1907, **356**, 122) obtained the latter compound by acting on diphenylketen with magnesium phenyl bromide, but for valid reasons he does not interpret the action on the basis of equation (*b*), where the keten is represented to act as if it contained a carbonyl group. Ketens are not ketones, their reactions being explained by the initial addition of reacting material to the ethylenic linking. But Staudinger's formulation,



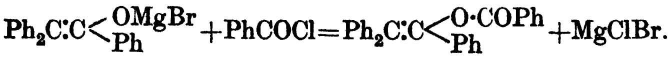
$$\mathrm{Ph_2C{:}CO+PhMgBr} \longrightarrow \underset{\mathrm{MgBr}}{\mathrm{Ph_2C}}\text{——}\underset{\mathrm{Ph}}{\mathrm{CO}} \longrightarrow \mathrm{Ph_2CH{\cdot}COPh} \longrightarrow \mathrm{Ph_2C{:}C}{<}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{Ph}\end{smallmatrix},$$

is nevertheless difficult to accept, since Kohler and others have shown that the Grignard reagent never adds on to an ethylenic linking in the 1 : 2-position. It may be noted in this connexion that Gilman and Heckert (*J. Amer. Chem. Soc.*, 1920, **42**, 1010) describe the action of benzoyl chloride on the additive compound of diphenylketen with magnesium phenyl bromide. If Staudinger's view were correct, then a 1 : 3-diketone, namely, diphenyldibenzoylmethane, should be produced :



$$\begin{smallmatrix}\mathrm{Ph}\\ \mathrm{Ph}\end{smallmatrix}{>}\underset{\mathrm{MgBr}}{\mathrm{C}}\text{——}\underset{\mathrm{Ph}}{\mathrm{CO}}+\mathrm{PhCOCl}=\begin{smallmatrix}\mathrm{Ph}\\ \mathrm{Ph}\end{smallmatrix}{>}\underset{\mathrm{COPh}}{\mathrm{C}}\text{——}\underset{\mathrm{Ph}}{\mathrm{CO}}+\mathrm{MgClBr}.$$

On the other hand, if the mechanism expressed in (*b*) be correct, then :

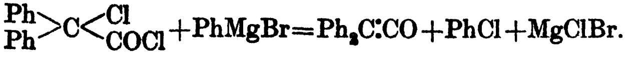


$$\mathrm{Ph_2C{:}C}{<}\begin{smallmatrix}\mathrm{OMgBr}\\ \mathrm{Ph}\end{smallmatrix}+\mathrm{PhCOCl}=\mathrm{Ph_2C{:}C}{<}\begin{smallmatrix}\mathrm{O{\cdot}COPh}\\ \mathrm{Ph}\end{smallmatrix}+\mathrm{MgClBr}.$$

Since the benzoate of triphenylvinyl alcohol was isolated, it was held by the American authors that the Grignard reagent does, after all, add on to the carbonyl group.

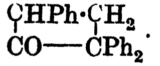
The assumption involved in equation (*a*) receives further support from the following considerations.

(1) Diphenyl is always formed in the preparation of magnesium phenyl bromide, but the amount of it can be lessened if an excess of magnesium is employed in preparing the reagent. Although this device was adopted throughout the present work, the amount of diphenyl isolated from the products of the reactions was greater than would have been expected had it been formed in the making of the reagent alone. On this ground equation (*a*), which involves the production of diphenyl, is preferred to the alternative scheme :



$$\begin{smallmatrix}\mathrm{Ph}\\ \mathrm{Ph}\end{smallmatrix}{>}\mathrm{C}{<}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{COCl}\end{smallmatrix}+\mathrm{PhMgBr}=\mathrm{Ph_2C{:}CO}+\mathrm{PhCl}+\mathrm{MgClBr}.$$

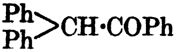
(2) When the experimental conditions were altered so that the Grignard reagent was added very slowly to an ice-cold ethereal solution of the chloro-chloride, the course of the reaction was quite different from that followed when the materials were added in the reverse order. The ethereal solution, after decomposition with ice and mineral acid, assumed an orange-red tint, and this is the appearance of diphenylketen. The main product of the action was in this case not triphenylvinyl alcohol but a plastic, brown, amorphous product, which gradually solidified to a hard mass resembling aldehyde-resin and doubtless consisted of polymerised diphenylketen. Staudinger mentions that diphenylketen resinifies completely at 250°, but although we did not at any point have the temperature so high as this, it is nevertheless likely that polymerisation may have been induced by catalytic influences, more especially since during the preparation of ketens by means of zinc it is occasionally found that the zinc haloid behaves as a polymerising agent. Since the conditions were such that in the early stages of the action there was a large excess of the acid chloride, the liberated keten, instead of combining with the Grignard reagent, may have undergone rapid polymerisation by the acid chloride itself, Staudinger having shown that acid chlorides, such as benzoyl chloride, polymerise diphenylketen. Staudinger and his pupils (*Ber.*, 1911, **44**, 530; *Annalen*, 1911, **384**, 109; *Ber.*, 1914, **47**, 41) have isolated three polymerides of diphenylketen melting respectively at 244—245°, 176°, and 188°, and of these three the constitution only of the first, diketotetraphenyl*cyclo*butane, has been determined. As a rule, however, diphenylketen gives resins when heated with condensing agents such as zinc chloride or sodium acetate. We extracted the small quantity of triphenylvinyl alcohol contained in our resin by means of petroleum, but no definite compound was obtained from the residue left after the extraction.

(3) Under the experimental conditions of (2), a product sparingly soluble in ether was obtained in relatively small amount. It melted at 256·5—257·5°, and its analysis suggested that it was an additive compound of diphenylketen and triphenylvinyl alcohol. It is well known that ketens have the property of adding on to unsaturated compounds with the formation of tetramethylene derivatives (although this conception of their structure is not accepted by Schröter), and Staudinger and Suter (*Ber.*, 1920, **53**, 1092) have shown that certain ethylenic compounds combine with diphenylketen to form what are regarded as *cyclo*butanone derivatives, styrene, for instance, giving the substance,  $\begin{array}{l}\mathrm{CHPh{\cdot}CH_2}\\ \mathrm{CO{-\!-}CPh_2}\end{array}$. Possibly, therefore, the compound isolated from the action of magnesium

phenyl bromide on diphenylchloroacetyl chloride has the formula $\begin{array}{l}\text{CPh}_2\cdot\text{CPh}\cdot\text{OH}\\ \text{CO—CPh}_2\end{array}$, but further work would be necessary before this point could be established definitely.

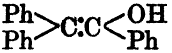
Constitution of Triphenylvinyl Alcohol.

Triphenylvinyl alcohol presents many interesting features from the point of view of desmotropism. Delacre (*Bull. Soc. chim.*, 1895, [iii], **13**, 857) and Gardeur (*Bull. Acad. roy. Belg.*, 1897, [iii], **34**, 67) formulated the compound obtained by the action of aluminium chloride on trichloroacetyl chloride and benzene as triphenylethanone (I).



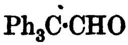
$\text{Ph}_2{>}\text{CH}\cdot\text{COPh}$

(I.)



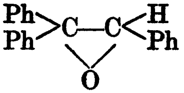
$\text{Ph}_2{>}\text{C:C}{<}^{\text{OH}}_{\text{Ph}}$

(II.)



$\text{Ph}_3\dot{\text{C}}\cdot\text{CHO}$

(III.)



(IV.)

Doubt was thrown on the validity of this formula by Biltz (*Ber.*, 1899, **32**, 650; *Annalen*, 1897, **296**, 242), whose arguments in favour of the structure (II) were so cogent that the designation triphenylvinyl alcohol has been almost universally adopted until quite recently. Biltz's grounds were briefly as follows. The compound is not triphenylacetaldehyde (III), since it forms neither an oxime nor a phenylhydrazone, and it does not undergo oxidation to triphenylacetic acid. The occurrence of benzophenone and benzoic acid as products of the oxidation pointed rather to (II) being correct; moreover, the addition of the elements of water effected by boiling with alcoholic sodium hydroxide gave diphenylmethane and benzoic acid. The analogy with diphenylvinyl alcohol (Breuer and Zincke, *Annalen*, 1879, **198**, 182; Claisen, *Ber.*, 1892, **25**, 1781) was close, since this substance on oxidation also gave benzophenone, whilst diphenylmethane was also formed by boiling with alcoholic potassium hydroxide. Moreover, if the replacement of two hydrogen atoms in vinyl alcohol by two phenyl groups directly attached to a carbon atom leads to the hydroxymethylene type, it is all the more likely that the introduction of a third phenyl group would impart still greater stability, and triphenylvinyl alcohol should not only be capable of a separate existence, but should be stable. The fourth possibility (IV) of triphenylethylene oxide is excluded by Biltz on the ground that the compound in question forms both an acetyl and a benzoyl derivative. The fact that triphenylvinyl alcohol does not give a urethane falls into line with the observation of Knoevenagel that many alcohols, for example, triphenylcarbinol, do not react with phenylcarbimide. Moreover, the hydroxylic structure of triphenylvinyl alcohol is supported by its absorption in the molten state of electric waves of high frequency.

The structure (II) was accepted by Staudinger (*loc. cit.*), Anschütz and Förster (*Annalen*, 1909, **368**, 89), Tiffeneau (*Compt. rend.*, 1908, **146**, 31), and by McKenzie and Wren (T., 1910, **97**, 474). On the other hand, Kohler (*Amer. Chem. J.*, 1906, **36**, 177) reverts to formula (I) on two grounds; the formation of acyl derivatives, on which the argument for (II) is largely based, is invalidated by the fact that ketones can be acylated (Lees, T., 1903, **83**, 152), whilst the behaviour towards magnesium ethyl bromide shows that the compound acts as a ketone, giving the corresponding tertiary alcohol. Orékhoff (*Bull. Soc. chim.*, 1919, [iv], **25**, 9, 186) examined the action of magnesium phenyl bromide and of magnesium benzyl chloride, and drew the same conclusion as Kohler.

Lately Meyer and Gottlieb-Billroth (*Ber.*, 1921, **54**, [*B*], 575) describe the conversion of phenyldiphenylene-ethanone into the isomeric phenyldiphenylenevinyl alcohol. Since the latter compound behaves as a normal enol, inasmuch as when freshly prepared it dissolves in cold dilute alkali, whilst its alcoholic solution decolorises bromine immediately, the conclusion is drawn that (I) is correct. The tendency for triphenylethanone to undergo enolisation is extremely slight, no enolisation being caused by alcoholic potassium hydroxide.

The chief grounds for reverting to (I) appear to be the insolubility in alkali and the behaviour towards Grignard reagents. An allelotropic mixture such as ethyl acetoacetate reacts towards Grignard reagents as if it were entirely enolic (Grignard, *Ann. Chim. Phys.*, 1902, [vii], **27**, 548; McKenzie, T., 1906, **89**, 365). Now triphenylvinyl alcohol, reacting according to (II), would give an additive compound when acted on by magnesium phenyl bromide, and the original substance would be regenerated on treatment of the additive compound with water. If the original substance were triphenylethanone, and if it had any tendency at all to undergo isomeric change into triphenylvinyl alcohol, the result would be the same, if triphenylethanone and triphenylvinyl alcohol were to behave like other isomerides that have been investigated from this point of view.

We accordingly repeated the action of magnesium phenyl bromide on triphenylvinyl alcohol, since the yield of *s*-tetraphenylethanol quoted by Orékhoff is smaller than would have been expected if one had to deal with triphenylethanone only, and since no details of the yield of tetraphenylpropan-β-ol are given by Orékhoff. We first employed magnesium phenyl bromide (3 mols.) for triphenylethanone (1 mol.), three times the calculated quantity; nevertheless, much of the original material was recovered. The action was more complete, however, when six molecular proportions of the Grignard reagent were employed. These results would point to the conclusion that if (I) is the correct formula, the reactivity of the carbonyl group is impaired just as it is in β-benzopinacolin. That we have to deal with a hydroxylic compound which under the influence of the Grignard reagent is slowly converted into a ketone which then reacts normally, is extremely improbable.

The balance of the evidence is certainly strongly in favour of the representation as triphenylethanone, but until further proof is given that the objections raised by Biltz are invalid, we do not go so far as Orékhoff and Meyer, who advocate that the term triphenylvinyl alcohol should now be deleted from the literature.

EXPERIMENTAL.

Action of Magnesium Phenyl Bromide on Diphenylchloroacetyl Chloride.

The following details, which are of importance for the successful preparation of diphenylchloroacetyl chloride, may be added to the descriptions of Bickel (*Ber.*, 1889, **22**, 1539) and of Staudinger (*Annalen*, 1907, **356**, 72). The oil resulting from the action of phosphorus pentachloride on benzilic acid is poured on to ice contained in a flat dish of such size that a thin layer of the acid chloride is exposed to the action of water. When, after frequent stirring, the oil has solidified, it is powdered under ice-cold water, and the whole allowed to remain overnight in the ice-chest. The solid is then separated, washed with water and with light petroleum, and dried over paraffin wax under diminished pressure. In a typical preparation, using 50 grams of phosphorus pentachloride (2 mols.) and 27·5 grams of benzilic acid (1 mol.), the yield of crude product was 30 grams. This was crystallised from 150 c.c. of light petroleum (b. p. 40—50°). The crystals melted at 48·5—49·5°, whereas Bickel gives 50°. The yield was 21 grams, 68 per cent. of the theoretical.

A solution of 40 grams of diphenylchloroacetyl chloride (1 mol.) in 100 c.c. of ether was gradually added within an interval of thirty-five minutes to the Grignard reagent prepared from 144 grams of bromobenzene (6 mols.), 400 c.c. of ether, and 48 grams of magnesium. The vigorous reaction was attended by the appearance of a green coloration in the solution. After boiling briskly for half-an-hour, the product was treated with ice and sulphuric acid in the usual manner. Overnight the colourless, crystalline solid in suspension between the two layers was separated and washed with a little ether, in which it is sparingly soluble. It amounted to 22 grams and melted at 134—135·5°. The ethereal layer was extracted with sodium hydroxide to remove the phenol and free acid present, the ether removed, and the residue distilled in a current of steam, when 13·3 grams of diphenyl were obtained. The residue, after removal of the diphenyl, was extracted with petroleum (b. p. 80—90°), and from the petroleum extract 7 grams of a product melting at 126—130° were obtained. The 29 grams of crude crystalline material were crystallised from petroleum (b. p. 80—105°), when colourless needles melting at 135—136° separated. They contained no halogen, and gave the brilliant emerald-green coloration with concentrated sulphuric acid which is characteristic of triphenylvinyl alcohol. The molecular weight determined in benzene solution by the boiling point method gave the value 267 (calc. 272) (Found: C=88·1; H=6·0. Calc., C=88·2; H=5·9 per cent.). The yield of pure product was 58 per cent. of the theoretical.

The action takes a different course when the Grignard reagent is added to the chloro-chloride under the following conditions. An ethereal solution of magnesium phenyl bromide prepared from 84 grams of bromobenzene (3½ mols.), 250 c.c. of ether, and 28 grams of magnesium, was gradually siphoned within an interval of four and a half hours into a solution of 40 grams of diphenylchloroacetyl chloride (1 mol.) in 100 c.c. of ether. The flask was immersed in ice-cold water during the addition of the chloro-chloride, when two layers gradually separated, the upper layer being pale brown in tint and the lower layer dark brown. After forty hours, the decomposition was conducted as before, and in this case the ethereal layer assumed a bright orange tint, and a yellow, oily layer separated between the ethereal and aqueous layers. After five days, this oily layer solidified. It amounted to 4·5 grams and apparently contained no triphenylvinyl alcohol, since it gave only a pale brown coloration with concentrated sulphuric acid. It was crystallised several times from benzene, from which it separated sluggishly in tiny prisms, and melted at 256·5—257·5°. It was free from halogen, and was sparingly soluble in ethyl alcohol, ether, or light petroleum (Found: C=88·0; H=5·8. $C_{34}H_{26}O_2$ requires C=87·6; H=5·6 per cent.).

The quantity of diphenyl obtained from the ethereal layer was 12·8 grams. The main product of the action amounted to 37 grams, and on cooling after the removal of the diphenyl it was plastic, but gradually set to a brown, hard, amorphous mass with the appearance of aldehyde-resin. All attempts to isolate a definite product from it failed. With concentrated sulphuric acid at the ordinary temperature a trace of the substance first became dark red, and on gently warming green. Apparently a trace of triphenylvinyl alcohol was present, but after extraction with boiling petroleum the residue still gave no definite compound.

Action of Magnesium Phenyl Iodide on Diphenylchloroacetyl Chloride.

Since Schmidlin has shown that the behaviour of magnesium phenyl bromide and magnesium phenyl iodide on triphenylacetyl chloride is different, and since Gomberg obtained pentaphenylethanol from β-benzopinacolin by using magnesium phenyl iodide in place of the bromide, the following experiments were carried out.

A solution of 13 grams of diphenylchloroacetyl chloride (1 mol.) in 50 c.c. of ether was acted on as before with magnesium phenyl iodide, prepared from 60 grams of phenyl iodide (6 mols.), the chloro-chloride being added to the Grignard reagent. After decomposition with ice and sulphuric acid, the solid in suspension was removed and found to consist of pure triphenylvinyl alcohol (4·1 grams). The ethereal layer contained dissolved iodine, which was removed with sodium hydrogen sulphite, and the free acids were removed as well as the diphenyl. The residue from the ether was a brown, plastic mass (7·2 grams), from which 4 grams of crude triphenylvinyl alcohol were extracted by boiling petroleum.

A solution of 13 grams of diphenylchloroacetyl chloride (1 mol.) in 50 c.c. of ether was siphoned within an interval of four hours into a solution of magnesium phenyl iodide prepared from 35 grams of phenyl iodide (3½ mols.). When the addition was complete, the upper layer was orange-red and the lower layer reddish-brown. On remaining at the ordinary temperature, iodine was gradually liberated. After ninety hours, the manipulation was conducted as before. The resin produced in this case amounted to 13 grams, and contained very little triphenylvinyl alcohol.

Action of Magnesium Phenyl Bromide on Triphenylvinyl Alcohol.

Assuming that triphenylvinyl alcohol reacts in its desmotropic form, triphenylethanone, only one molecular proportion of magnesium phenyl bromide would be required to form the additive compound, $Ph_2CH{\cdot}CPh_2(OMgBr)$. Although in the following experiment an excess (3 mols.) of Grignard reagent was employed, a considerable quantity of the triphenylvinyl alcohol was recovered.

Powdered triphenylvinyl alcohol (24 grams, 1 mol.), prepared by the dehydration of triphenylethylene glycol, was gradually added within an interval of twenty minutes to the Grignard reagent prepared from 42 grams of bromobenzene (3 mols.). Heating was then carried out for four hours, and the product decomposed as usual. The solid in suspension amounted to 26 grams and consisted largely of triphenylvinyl alcohol, of which 9 grams of the pure product were isolated by extraction with petroleum (b. p. 80—90°). The residue after extraction with petroleum was crystallised from benzene, when 3 grams of ααββ-tetraphenylethyl alcohol separated in colourless needles which melted at 232·5—233°, whereas Orékhoff (*loc. cit.*) gives 235—236° (Found: C=88·9; H=6·5. Calc., C=89·1; H=6·3 per cent.).

An additional 2 grams were also isolated, whilst from the ethereal solution in which the solid had been suspended a small quantity of triphenylvinyl alcohol was also obtained.

When a larger excess of magnesium phenyl bromide was employed and when the heating after the addition of the reagent was prolonged for seven hours, the proportion of triphenylvinyl alcohol in the product was much smaller than was the case in the experiment just quoted. Twenty grams of triphenylvinyl alcohol (1 mol.) were heated for seven hours with a solution of magnesium phenyl bromide prepared from 70 grams of bromobenzene (6 mols.). The amount of solid which remained undissolved after the addition of ice and sulphuric acid was in this case only 8·7 grams, and the proportion of ααββ-tetraphenylethyl alcohol in this solid product was much greater than before. The product from the ethereal solution contained very little triphenylvinyl alcohol.

The authors desire to express their thanks to the Carnegie Trust for a grant in aid of this research.

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University of St. Andrews.

[*Received, June 1st*, 1921.]

CXXV.—*Inorganic Complex Salts. Part I. Potassium Ferrioxalate and Potassium Cobaltimalonate.*

By William Thomas.

Potassium Ferrioxalate, $[Fe(C_2O_4)_3]K_3,3H_2O$.

The corresponding complex salts of cobalt, chromium, rhodium, and iridium have been resolved into optically active components, and it was considered interesting to try to obtain the active antipodes of the complex ferri-salt.

The salt was prepared by dissolving freshly precipitated ferric hydroxide in a solution containing the necessary amount of potassium hydrogen oxalate at 35—40°. The hydroxide dissolved to form a beautiful green solution, which on keeping gave well-developed, monoclinic crystals of the ferri-salt.

When exposed to light, potassium ferrioxalate decomposes very readily according to the equation,

$$2[Fe(C_2O_4)_3]K_3=2[Fe(C_2O_4)_2]K_2+K_2C_2O_4+2CO_2,$$

and yellow crystals of potassium ferro-oxalate are gradually deposited from the solution. For this reason the preparation and all experiments with the complex salt were carried out in the dark.

Attempts to resolve the ferrioxalate by combination with the alkaloid bases were unsuccessful. The tristrychnine salt was prepared and its solution (which was green) was placed in a dark, cool place. In twenty-four hours the solution had become colourless and a large crop of yellow crystals had been deposited. These were found to be distrychnine ferro-oxalate. The tristrychnine salt is evidently much more unstable than the corresponding potassium salt. The same results were obtained with brucine and cinchonine as active bases. To prevent this reduction, the method of fractional precipitation was tried. The strengths of the potassium ferrioxalate and alkaloid sulphate solutions were so chosen that on mixing about one-fifth of the alkaloid complex salt was precipitated. This, on conversion into the potassium salt by treatment with potassium iodide, again gave negative results.

For the resolution of a racemic compound by combination with an active molecule, the necessary conditions are (1) stability of the intermediate compound, and (2) favourable solubility relationship. The above experiments show that the alkaloid ferrioxalates satisfy neither of these conditions. The instability of the intermediate compounds in the above cases is easily explained by the fact that the alkaloids are (1) weak bases and (2) readily oxidised. Experiments were next carried out with α-phenylethylamine as the active base. A solution of potassium ferrioxalate was mixed with a solution containing the equivalent amount of the hydrochloride of the base; this was then subjected to fractional crystallisation in the dark. Green crystals of the ferri-salt were gradually deposited. The conversion of this salt into the potassium salt could not be carried out by the addition of potassium hydroxide solution, as this reagent precipitated ferric hydroxide. To the solution of the phenylethylamine salt was added a solution of barium chloride; this produced a green precipitate of barium ferrioxalate, $[Fe(C_2O_4)_3]_2Ba_3$, which was converted into the potassium salt by shaking with a solution of potassium sulphate. A solution of the potassium salt so formed was found to be inactive.

The second fraction was dissolved in water and examined polarimetrically. This was a solution of the *l*-phenylethylamine salt of the complex. It was found to be lævorotatory, but its activity rapidly diminished to zero. Active phenylethylamine has a very low rotatory power, $[\alpha]_D$ 25·65°. In the above dilute solution its rotation would be negligible and the rapid change observed in the activity is evidently due to the rapid racemisation of the ferri-salt.

The next fraction was rapidly converted by the above method into the potassium salt. It was found to be optically active, but the activity was soon lost, as the following readings show.

0·5 Per cent. solution.	Time (mins.).	Observed rotation.	$[M]_D$.
	15	0·20°	874°
	30	0·10	437
	45	0·04	175
	60	zero	—

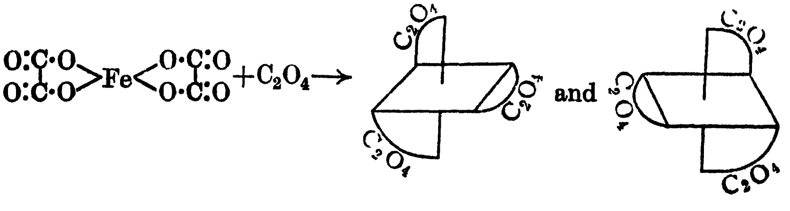
Initial $[M]_D$ (calculated) = 1748°.

A solution of the potassium salt loses one-half of its rotatory power in fifteen minutes. Further fractions were collected and they were all found to contain the *l*-complex salt. This is a natural result of the rapid racemisation of the active complex salt. We have in the solution the following equilibrium: A B $\rightleftharpoons$ A′B (A = *l*-complex salt, A′ = *d*-complex salt, B = *l*-base). A B is less soluble than A′B and therefore crystallises first, this disturbs the equilibrium in the solution and the change A′B ⟶ A B goes on until equilibrium is restored. More A B is deposited and so on, until finally the whole of A′B has been converted into the one active form. *l*-Phenylethylamine gives the *l*-complex salt and the *d*-base gives the *d*-complex salt. Similar results were obtained by Pope and Peachey in their resolution of methylethyl-*n*-propylstannic iodide (P., 1900, **16**, 52).

Racemisation is probably due to a partial breaking up of the complex:

$$[Fe(C_2O_4)_3] \longrightarrow [Fe(C_2O_4)_2]+C_2O_4.$$

The two remaining oxalato-groups would lie in one plane and the third oxalato-group could re-enter in two ways to form either of the enantiomorphous forms,



$$\begin{matrix}O:C\cdot O\\ |\\ O:C\cdot O\end{matrix}>Fe<\begin{matrix}O\cdot C:O\\ |\\ O\cdot C:O\end{matrix}+C_2O_4\longrightarrow$$

This detachment of one oxalato-group may be caused by:

(1) Ionisation. These complex salts with complex anions ionise primarily according to equation (*a*).

$$(a)\ [Fe(C_2O_4)_3]K_3 \longrightarrow [Fe(C_2O_4)_3]''' + 3K^{\cdot}.$$

Secondary ionisation also sets in as represented by equation (*b*).

$$(b)\ [Fe(C_2O_4)_3]''' \longrightarrow [Fe(C_2O_4)_2]' + C_2O_4''.$$

As a matter of fact, tests prove the presence of metallic ions in aqueous solutions of these complex salts, for example, a solution of ammonium sulphide produces an immediate precipitate of the metallic sulphide. If potassium hydroxide is added to a solution of potassium cobaltioxalate, there will be gradually formed a precipitate of cobalt hydroxide. In the case of potassium ferrioxalate the formation of a precipitate of ferric hydroxide is much more rapid. This points to the fact that ionisation proceeds much further in the case of potassium ferrioxalate than in that of the corresponding cobalti-compound. This might explain the rapid racemisation of the ferri-salt.

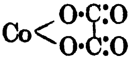
With a view to prevent this ionisation, the complex salt was dissolved in a mixture of acetone and water. Attempts were also made to suppress ionisation by working in a solvent containing a common ion (an aqueous solution of potassium chloride). In neither of these cases was the rate of racemisation decreased.

(2) The ferri-salt undergoes spontaneous reduction to the ferro-salt. This naturally involves the loss of optical activity, but racemisation proceeds at a much greater rate than the reduction. It is possible that there is a reversible reaction—oxidation and reduction—going on in the solution. To overcome this, determinations of activity were carried out in hydrogen peroxide as solvent. Racemisation, however, was not influenced.

Further experiments are being carried out to study this phenomenon.

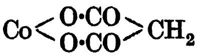
Potassium Cobaltimalonate, $[Co(C_3H_2O_4)_3]K_3,3H_2O$.

The stability of these complex salts depends very largely on the number of atoms in the rings which the central atom forms with the dibasic acids (compare Werner, *Annalen*, 1912, **386**, 42). In the oxalato-complexes the ring contains five atoms, whilst there are six atoms in the ring of the malonato-compounds, and the former are much more stable than the latter. All attempts to prepare the succinato-complexes of the type $[MeX_3]$ have so far been unsuccessful; in these the ring would contain seven atoms.



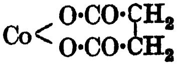
$$\mathrm{Co}<\begin{matrix}\mathrm{O{\cdot}C{:}O}\\ |\\ \mathrm{O{\cdot}C{:}O}\end{matrix}$$

Oxalato-.



$$\mathrm{Co}<\begin{matrix}\mathrm{O{\cdot}CO}\\ \mathrm{O{\cdot}CO}\end{matrix}>\mathrm{CH_2}$$

Malonato-



$$\mathrm{Co}<\begin{matrix}\mathrm{O{\cdot}CO{\cdot}CH_2}\\ |\\ \mathrm{O{\cdot}CO{\cdot}CH_2}\end{matrix}$$

Succinato- (not prepared).

The cobaltimalonate has not been described, and it was considered interesting to study its preparation and properties.

Attempts were made to prepare it by the method employed for the corresponding oxalate, but the yield was at first very poor. By slight modifications in the procedure, however, the yield was very much increased. Cobalt carbonate was dissolved in a saturated solution containing the necessary amount of potassium hydrogen malonate. The pink solution was cooled below 0°, excess of lead peroxide added, and 50 per cent. acetic acid poured into the solution very gradually, the whole being stirred continuously. The solution was filtered and to the dark green filtrate was added three times its volume of 97 per cent. alcohol. The precipitate was dissolved in water and reprecipitated with alcohol. The cobaltimalonate was thus obtained as a beautiful, dark green, crystalline precipitate; yield 12 grams from 10 grams of cobalt carbonate (Found: C=19·91; H=2·21; Co=10·89.

$$[\mathrm{Co(C_3H_2O_4)_3]K_3,3H_2O}$$

requires C=19·99; H=2·15; Co=10·92 per cent.).

The complex salt is much more unstable than the corresponding oxalato-compound. A solution which had been kept in the dark for twenty-four hours deposited a large crop of pink crystals and the dark green solution had become colourless. The cobalti-salt had thus been reduced to the cobalto-salt, which is but sparingly soluble in water (compare the cobaltioxalate). With a view to prevent this reduction and to obtain measurable crystals, the complex salt was dissolved in a solution of hydrogen peroxide, which was placed in a cool, dark place. The presence of hydrogen peroxide retarded the reduction; the dark green colour of the solution, however, gradually disappeared and pink crystals of the cobalto-salt were again deposited.

The sodium and ammonium salts were prepared, but were found to be more unstable than the potassium salt.

Attempts to resolve the complex malonate have so far been unsuccessful. The alkaloid salts are too unstable for fractional crystallisation, and negative results were obtained by the method of fractional precipitation. Combination with phenylethylamine as the active base also gave no activity. Further attempts will be made under different conditions.

The author would like to express his gratitude to Professor Sir William Pope and to Dr. W. H. Mills for the interest they have taken in this work, and for their valuable advice and criticism. While carrying out this research, he has held an 1851 Exhibition Scholarship and gratefully acknowledges this assistance.

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CAMBRIDGE. [*Received, June 16th, 1921.*]

CXXVI.—*A New Method for Determining the Volatile Matter yielded by Coals up to Various Temperatures.*

By WILLIAM ARTHUR BONE and LEONARD SILVER.

IT has always been considered important, in connexion with the so-called " proximate analysis " of coals, to determine the amounts of volatile matter expelled from them under certain prescribed conditions. Such determinations, if properly carried out, would be capable of giving results of scientific as well as commercial value, inasmuch as they are useful in connexion with the classification of coals. The value of a particular test depends, however, largely upon the trustworthiness of the information it affords as to (*a*) the precise amount of volatile matter expelled from the coal under given temperature conditions, and (*b*) the character of the carbonaceous residue obtained. However, as the amount of volatile matter yielded by a given coal varies considerably with the temperature at which it is carbonised, it is obvious that, unless the temperature conditions of a test are carefully attended to, its quantitative value may be small. Also, unless the heating operation is carried out in such a manner as will effectually eliminate, or at least render negligible, the influence of air, the results may be misleading.

Hitherto, it has been customary to employ one or other of the two following methods. The first was recommended in 1899 by the American Chemical Society (*J. Amer. Chem. Soc.*, 1899, **21**, 1122), and is known as the " American Method " ; it was originally prescribed as follows :

" Place 1 gram of fresh undried powdered coal in a platinum crucible, weighing 20 to 30 grams, and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. To find the Volatile Combustible Matter subtract the percentage of moisture from the loss found here."

A similar test was adopted by the chemists responsible for the Canadian Coal Survey, the only difference being that it was carried out on the *dry*, instead of the *undried*, coal (*vide* "An Investigation of the Coals of Canada," Vol. II., p. 134, by J. B. Porter, R. J. Durley, and others, issued in 1912 by the Canadian Department of Mines). The chief objections which have been urged against the method are (1) that the temperature conditions are not sufficiently defined, (2) that the influence of air is not sufficiently eliminated, (3) that the employment of a platinum crucible introduces catalytic influences to an unknown extent, and (4) that it does not enable a trustworthy judgment to be formed about the coking properties of a coal.

The second method is known as the "Crucible Test," and is usually carried out by carbonising 20 grams of the dried coal in a No. 3 Morgan fireclay crucible fitted with a suitable lid at a temperature of 900° in a muffle furnace, the heating being continued for ten minutes after the evolution of inflammable gases has entirely ceased (for further details *vide* W. A. Bone, "Coal and its Scientific Uses," p. 57). This test is capable of giving valuable information as to the coking properties of the coal, and inasmuch as it can always be carried out at a definite temperature (900° being usually selected), it is on the whole perhaps preferable to the "American" method. Neither of the methods is, however, capable of the degree of precision which is nowadays needed for purposes of scientific classification.

Some years ago, Lessing (*J. Soc. Chem. Ind.*, 1912, **31**, 465) described "A New Apparatus for the Coking Test of Coal" which obviated some of the disadvantages of the crucible test. One gram of the powdered coal was electrically heated, under slight pressure, for between five and seven minutes, in a long, vertical quartz tube, of about 10 mm. diameter, open at the upper end. The heating arrangements were such that most of the heat was concentrated at the bottom of the tube and on its walls for a distance of 15 mm. up; the upper part of it, being exposed to the air, was kept relatively cool. "The practical value of the apparatus" was said by its author "to lie principally in the fact that the coke obtained in it brings out the peculiarities of a coal in a much more striking fashion than does the coke in the crucible test" (*ibid.*, p. 466).

But, as regards the accurate determination of the volatile matter in a coal, it seems to us to be open to criticism in that (*a*) air is not excluded, (*b*) there is nothing to indicate with certainty the precise moment when the expulsion of volatile matter ceases, and (*c*) the temperature to which the coal is heated during the test can scarcely be regulated with sufficient accuracy.

In the course of an investigation which one of us was asked to carry out upon a certain seam of anthracitic coal, it was desired to obtain accurate information concerning a suspected gradual transition in the character of the coal in both vertical and horizontal directions in the seam. The extent and direction of the suspected change would be shown by corresponding variations in the yields of volatile matter obtained from samples taken at different parts of the seam. Since, however, the total variation in such yields throughout the whole of the seam was not expected to amount to more than two or three per cent., it will be seen that the degree of accuracy required in the determinations was considerably more than could be ensured from the employment of any of the methods already referred to. Moreover, on trying the first two methods, they utterly failed to give results of any value for the purpose in view.

Accordingly, a new method had to be devised and, after extended trials, the following was ultimately adopted. As subsequent experience with it has shown its applicability to all types of coal, we propose now to describe it in the hope that other workers may find it useful.

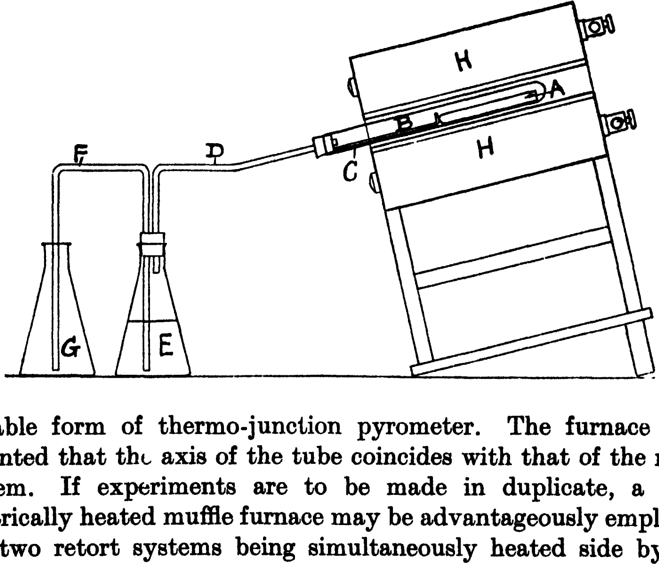
EXPERIMENTAL.

The New Method.—The new method consists essentially in carbonising a weighed quantity of the finely divided coal at a definite temperature in a silica tube from which air is excluded during the operation. The tube is heated in an electric resistance-furnace which can easily be maintained within a few degrees of the desired experimental temperature, which is read by means of a suitable thermo-couple device. The general arrangement of the apparatus is shown in the accompanying diagram.

The coal, having previously been dried and ground so as to pass a sieve having 30 meshes to the linear inch, is quickly weighed out into a small silica tube, *A* (12 cm. × 1·5 cm.), which is closed at one end. The quantity of coal taken (usually 5 grams) should about half-fill this tube, which is then pushed, open end first, to the far end of the larger silica tube, *B* (30 cm. × 2·5 cm.). Throughout the ensuing test this "retort" part of the apparatus is kept in an inclined position so as to retain the coal in the smaller tube, which is held towards the closed end of the larger one by means of the silica rod, *C*, as shown in the diagram. Into the mouth of *B* is fitted a rubber stopper carrying a glass delivery tube, *D*, communicating with the upper part of the flask, *E*, which is three-quarters filled with water. A second glass tube, *F*, passes from near the bottom of *E* to near that of a second flask, *G*, which is open to the outside atmosphere and, at the outset of the experiment, contains nothing but air.

All these preparations having been completed, the retort system is thereupon gradually introduced into a nichrome-wound and electrically heated tube furnace, *H H*, of suitable dimensions, which has previously been raised throughout a length of at least 30 cm. to a uniformly constant temperature of 900°, as indicated by any suitable form of thermo-junction pyrometer. The furnace is so mounted that the axis of the tube coincides with that of the retort system. If experiments are to be made in duplicate, a small electrically heated muffle furnace may be advantageously employed, the two retort systems being simultaneously heated side by side in it. In either case, it is preferable that the furnace body be suitably mounted on small wheels, so that it may be gradually slid over the retort system; but, for the sake of simplicity, this adjunct is not shown in the diagram.

FIG. 1.



As soon as the retort system has attained the temperature of the furnace, the volatile constituents of the coal are rapidly expelled, driving the air out of the tube before them. The water in the flask *E* is soon displaced into flask *G* by the issuing gas, which then bubbles through the water-seal in *G* into the open air. The rate of evolution of the gas can thus be gauged, and the end of the carbonisation is indicated by its cessation. The time taken for the completion of the test is usually about forty minutes, being rather longer for anthracitic than for most bituminous coals. If, however, the coal contains a high percentage of volatile matter, care must be taken to draw the furnace very gradually over the retort system.

As soon as the expulsion of gas from the coal has ceased, the retort system is carefully withdrawn from the furnace and allowed to cool while still connected with the flasks *E* and *G*. The ensuing contraction of the gases in the apparatus causes water to be sucked back from *G* into *E*, but no air can be drawn into the system. When the retort is cool enough to be handled, the inner tube is carefully removed, contact with any remains of tarry matter in the lower part of the outer tube being avoided; it is then cooled in a vacuum desiccator, and finally weighed as rapidly as possible. The loss in weight gives the yield of volatile matter at 900°.

General Applicability of the Method.—How entirely satisfactory the method proved to be when applied to the particular class of anthracitic coals for which it was originally devised may be judged from the following tabulated results, in which the Roman numerals indicate the actual sequence of the various samples in the seam under investigation; attention is directed both to the close agreement between duplicate determinations and to the unmistakable way in which the continuous and gradual change in the character of the coal along the seam is brought out.

TABLE I.

Results showing the gradual Change in the Character of an Anthracitic Coal along a particular Seam.

Coal Sample No.	Percentage of volatiles at 900° found in different experiments.				Mean.
I	11·90	11·91	11·96	12·00	11·94
II	11·59		11·69		11·65
III	11·54		11·67		11·60
IV	11·38		11·30		11·34
V	11·01		11·08		11·05
VI	10·79		10·86		10·83
VII	10·70		10·74		10·72
VIII	10·60		10·62		10·61
IX	10·01		10·03		10·02
X	9·88		9·91		9·90

At a later stage of the investigation it was found that satisfactory results, showing a high degree of concordance, could be obtained with almost every class of coal. The method of heating, however, required to be modified in certain cases. For example, one type of coal was found to decompose at red heat with considerable violence; so much so that when it was carbonised in a fireclay crucible by the ordinary "crucible method" there resulted an explosion powerful enough to fracture the crucible. The difficulty was overcome by putting the retort system in the furnace when its temperature was 500°, and then gradually raising the temperature until 900° was attained in about an hour and a half. This method of slow heating also proved successful in the case of coals with a very high percentage of volatiles, where there was a risk of loss through the rapid evolution of gas blowing some of the finer coal out of the tube.

Comparison of the New with Former Methods.—In order to ascertain how results obtained by our new method compare with those yielded by the "American" and "Crucible" tests, respectively, a series of trials was made in which samples representative of different classes of coal were carbonised by each of the three methods. The results obtained are tabulated below, together with the differences observed in the results of duplicate tests by each method :

TABLE II.

Comparison of Results obtained by the different Methods.

Coal.	Percentage of volatiles at 900° as determined by			Differences between duplicate determinations in		
	(*a*) Silica tube.	(*b*) American method.	(*c*) Crucible method.	(*a*)	(*b*)	(*c*)
1. Welsh anthracitic	11·95	12·82	13·59	0·10	0·20	1·12
2. Welsh steam	17·76	18·11	18·66	0·11	0·02	0·28
3. Welsh coking ...	19·93	21·19	20·34	0·07	0·06	0·04
4. Durham coking ...	26·29	26·71	24·62	0·22	0·37	0·04
5. Brodsworth soft	37·43	40·24	36·64	0·06	0·48	0·16
6. Bullcroft soft	39·86	41·35	39·52	0·02	1·36	0·16
7. Peruvian	37·60	36·68	35·64	0·36	0·44	1·64
8. Nigerian sub-bituminous	41·32	43·23	38·94	0·05	0·06	0·04
9. Cannel (S. Wales)	54·05	56·42	52·92	0·02	0·68	0·88

The above results show that, in general (1) the silica tube method gives values intermediate between those given by the other two, the American method usually giving a higher, and the crucible assay method a lower figure, and (2) the degree of concordance is greater for the silica tube method than in either of the others.

The figures obtained by the American method are probably as a rule too high for the following reasons : (1) the temperature attained may rise beyond 900°, and (2) the evolution of the gas is so rapid that small particles of the coal are apt to be carried out of the crucible. Also, the results may be affected by the catalytic action of the platinum.

Judging from our experiments, the crucible method gives results which, whilst usually too high for coals yielding less than about 20 per cent. of " volatiles," are almost invariably too low in the case of their yielding more than that percentage. The reason for this rather curious circumstance became apparent during our investigation of the silica tube method. It was then found that whilst the evolution of gas was fairly rapid during the early stages, it became very slow towards the end of the carbonisation, and continued to be so for a considerable time before finally ceasing; the whole process required about forty minutes for its completion. Now in the crucible method, as ordinarily carried out, the period of heating usually extends over about thirty minutes for a 20 gram charge; and in the cases of coals containing more than about 20 per cent. of volatiles, it seems that the evolution of gas would usually continue for longer than ten minutes after the disappearance of visible flame, when the crucibles are withdrawn from the furnace. To leave them in long enough to complete the carbonisation would entail the risk of appreciable loss by oxidation through air coming in contact with the topmost layer of the carbonaceous residue (coke); hence the practice of withdrawing them (as it now seems) somewhat prematurely, with consequent low results, in such cases. On the other hand, when coals yielding less than about 20 per cent. of " volatile " at 900° are tested, the usual time allowed in the furnace is sufficient both to complete the carbonisation, and also to allow of some oxidation of the carbonaceous residue, so giving results which are too high.

It would appear, therefore, that the determination of the yield of " volatiles " at 900°, or any other selected temperature, can be carried out with greater accuracy by the new method described in this paper than by either of the other two in common use. The chief advantages to be gained by using the new method may be summarised as follows:

(1) The temperature conditions are more accurately known, and can be regulated to a nicety. This applies also to any temperature that may be selected as the desired uppermost limit.

(2) The rate of heating of the charge is under perfect control.

(3) The carbonisation is carried out in an inert atmosphere, and there is no risk of oxidation.

(4) Completeness of carbonisation at any selected temperature is assured, since the heating is always continued until no more bubbles of gas are evolved.

(5) The volatile products, more especially the gas, can be collected for examination, if desired, by attaching to the retort system any suitable arrangement of collecting and measuring vessels.

(6) If the carbonaceous residue is sufficiently coherent to form a

coke, the latter is obtained in a cylindrical form which is very convenient for subsequent examination.

In conclusion, we desire to state that this investigation has formed part of the work carried out by one of us during his tenure of a Salters' Fellowship at the Imperial College of Science and Technology, South Kensington.

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CXXVII.—*The Mechanism of the Oxidation of Drying Oils as Elucidated by a Study of the True Oxygen Absorption. Part I. Linseed Oil and its Fatty Acids.*

By SAMUEL COFFEY.

IT has been known for centuries that linseed oil on exposure to air, especially in thin films, gradually alters and finally " sets " to a tough elastic product, which is now known as linoxyn.

During this process of " drying," which is due to atmospheric oxidation, the oil increases in weight, and it has been found by many investigators that the maximum increase in weight varies considerably, from 13 to 25 per cent., 18 per cent. being the value usually obtained. Further experiments have been made to obtain the oxidation curve for linseed oil by weighing a glass plate on which is spread a thin film of the oil (0·15 gram per 100 sq. cm.), allowing the oil to oxidise and weighing at intervals of, say, ten hours. The results of such experiments show that at first there is a period of induction, during which there is very little oxidation; then follows a relatively rapid increase in weight, which rises to a maximum, after which there is a slow decrease in weight. This maximum percentage increase in weight is called the oxygen value, but for reasons to be given it should be called the apparent oxygen value. The real oxygen absorption is considerably greater than the maximum increase in weight because, while oxygen is being absorbed, volatile decomposition products are being evolved. Hence the apparent oxygen value is simply the point where the rate of loss of volatile matter is equal to the rate of oxygen absorption. As has been shown recently, this value is dependent on the temperature at which the oxidation takes place. Although Mulder ("Die Chemie der austrockenden Oele," Berlin, 1867) directed attention to this and examined the volatile products more than half a century ago, this important fact has been repeatedly overlooked by more recent investigators. Borries ("Dissert., Leipzig Lab. f. angew. Chem.," 1903) obtained true oxygen values, but apparently the only true oxygen absorption curves are those of Friend (*Proc. Paint Varnish Soc.*, May, 1914), who estimated the volatile products of oxidation. Friend's experiments, however, were carried out at the ordinary temperature and seventy days were required to complete one estimation; even then, apparently, oxidation was not complete. His curves (see "The Chemistry of Linseed Oil," J. N. Friend, 1917, p. 49) showed the marked difference between the apparent and true oxygen absorptions, but they only indicated the general shape of the curves.

Apart from the results of Friend, there is scarcely any evidence as to the mechanism of the oxidation, as the curves give only the combined results of two processes, the oxidation and the loss of volatile products. Further, as the oxidation is so slow at the ordinary temperature, most of the work has been done in the presence of "driers," which were assumed to be catalysts; as will be shown in a subsequent contribution to this subject, such results are not comparable with those obtained with oil alone. The volatile products have received much attention during recent years, and the following conclusions are fairly well established. Mulder (*loc. cit.*) found that water, carbon dioxide, and acetic acid constituted the main products, along with small quantities of formic and acrylic acids. Traces of butyric acid have been detected by Sacc (*Annalen*, 1844, **51**, 213) and Gardner (*Oil and Colour Trades Journ.*, 1914, **45**, 1000), whilst acraldehyde has been detected in traces by Salway (T., 1916, **109**, 138) in the earlier stages of the reaction, and carbon monoxide by King (*J. Ind. Eng. Chem.*, 1915, **7**, 502). No quantitative data, however, appear to exist as to the proportions of the main volatile products.

The constitution of linoxyn, based as it is on the work done on the apparent oxygen absorption, and on the supposition that driers act as catalysts, is in some degree conjecture, and the views of Fahrion (*Zeitsch. angew. Chem.*, 1910, **23**, 722), and of Orloff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 658), although highly suggestive, need not therefore be discussed in detail.

The aim of this research was to obtain true oxygen absorptions and true oxidation curves, and to find the connexion between these and the volatile products and so to form some idea of the constitution of linoxyn.

EXPERIMENTAL.

The oil used was guaranteed to be pure, unadulterated, raw linseed oil and the following constants confirmed its quality: iodine value (Wijs) 184·1; saponification value 193·6 (grams of KOH per kilo.); acid value 5·24 (grams of KOH per kilo.); glycerol (from above) 10·20, (by the acetin method) 10·30 per cent.; glyceryl (C_3H_5) 4·3; acids (by direct weighing) 95·63; total 99·93 per cent.

The absorption of oxygen might have been followed by leading gas through a known quantity of oil and then through weighed tubes for the absorption of the volatile products (Friend, *loc. cit.*). However, as shown by Genthe (*Zeitsch. angew. Chem.*, 1906, **19**, 2087), for complete and uniform oxidation the oil must be in a thin film, and the volatile products must be rapidly absorbed. In this investigation a modified form of Genthe's apparatus was used.

The film of oil was obtained by soaking a filter-paper (11 cm. diameter) with a known volume of a "standard" solution of the oil in light petroleum (b. p. 40—60°). The filter-paper was placed in the apparatus, which was then closed, completely filled with hydrogen, and placed in a thermostat at 100°, this temperature being chosen because it was thus possible to complete an estimation in six to seven hours. When the temperature of the film of oil was constant, the apparatus was quickly filled with oxygen (time required, one minute) and manometer readings were taken at intervals. The volume of the apparatus was determined by measuring the volume of water required to fill it, corrections being applied for the volume of the absorbents and manometer leads.

The most satisfactory absorbents were found to be sulphuric acid and solid potassium or sodium hydroxide.

In the early experiments irregular results were obtained, which were due to the choking of the tubes containing the absorbents owing to the action of the volatile products.

It was evident that a larger absorbing surface was required, and the final apparatus was as follows: Broken pumice, soaked with sulphuric acid, was placed at the bottom of a 500 c.c. flask, care being taken not to "wet" the neck. In order to expose a large surface of alkali, a stick of sodium hydroxide was wrapped in copper gauze and one end of the roll was fitted into a glass cup. The roll was lowered cup first into the flask, and the filter-paper containing the oil film was then suspended in the neck from a hook in the stopper. The apparatus was then filled with hydrogen; the subsequent procedure was as before. A further improvement was made in measuring the volume of the apparatus by a method based on the principle of Joly's volumenometer. The volume, V, of the apparatus is given by the equation

$$V = \frac{p_0 - p_2}{p_2 - p_1} \, . \, v,$$

where v is the volume of the auxiliary bulb (J) attached to the apparatus, and p_0, p_1, and p_2 are, respectively, the pressures in the bulb, in the apparatus, and in the latter when connected with J. The gas in the auxiliary bulb must be free from carbon dioxide and water vapour; in practice, the method of filling with water gave quite as accurate results.

Blank experiments with this apparatus showed that no absorption took place by oxidation of the paper, etc., and the efficiency of the absorbents was proved by admitting one to two per cent. of carbon dioxide and water vapour, when complete absorption occurred in sixty seconds.

In Table I are given the results obtained with the linseed oil.

TABLE I.

Linseed Oil.

Weight of oil. Gram.	Oxygen absorption. Per cent.
0·6533	28·6
0·6380	28·9
0·4446	28·1
0·5726	29·2
0·7172	28·7
0·4630	29·0
Mean	28·7

TABLE II.

Fatty Acids.

Weight of acids. Gram.	Oxygen absorption. Per cent.
0·3450	30·06
0·3725	30·20
0·3450	30·05
0·3450	30·06
Mean	30·09

Although the amount of oil varies considerably, it will be noticed that the results are constant; the extreme values differ by 2 per cent. from the mean, whilst the error in most cases is less than 1 per cent.

The fatty acids of the linseed oil were also examined in a similar manner to ascertain whether the glyceryl radicle had any effect on the mechanism of the oxidation; the results obtained are given in Table II.

The results are quite constant and clearly show that the true oxygen absorption, unlike the apparent oxygen value, is a definite quantity; it is also much higher than the values hitherto obtained for the so-called oxygen value.

True Oxygen Absorption Curves.

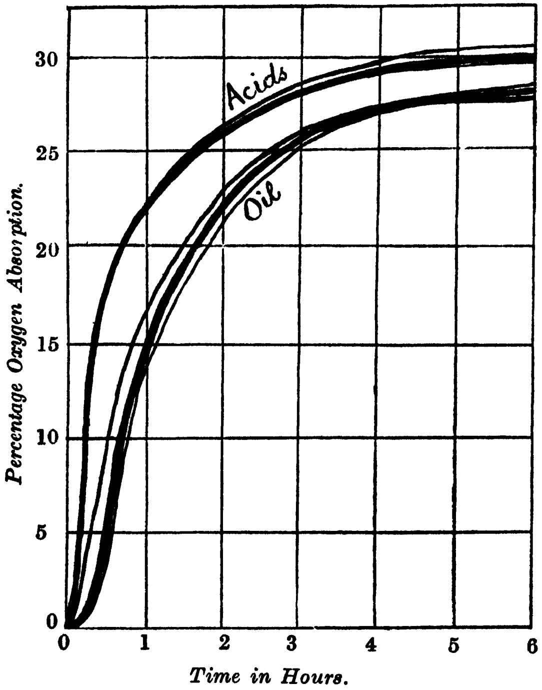
The oxidation of linseed oil in an atmosphere of constant oxygen concentration is a heterogeneous reaction. When oxidation occurs in thin films, the reaction curve for a pure individual substance, as is well known, approximates to that of a unimolecular, non-reversible reaction. This was appreciated long ago, and many attempts have been made to bring the apparent oxygen absorption curves into conformity with a logarithmic curve; formulæ have been put forward from time to time, such as

$$k=\frac{1}{t(A+B)}\cdot\log_e\left(\frac{A}{A-x}\cdot\frac{B+x}{B}\right)$$

(Orloff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 658; 1911, **43**, 1509), where A is the total apparent oxygen absorption and B is a constant.

Fig. 1.

Mean and Extreme Oxidation Curves for Linseed Oil and Fatty Acids.



Since linseed oil is a complex mixture of substances which will certainly oxidise at different rates, and since hitherto only apparent oxygen values have been used, it would be quite fortuitous were these curves logarithmic.

Fig. 1 shows the oxidation curves obtained for linseed oil and the fatty acids, and Table III a typical set of readings from which the curves were obtained. These curves show that at first there is a period of induction which, in the case of linseed oil, lasts for almost fifteen minutes; then a moderately rapid oxidation commences, but gradually the velocity diminishes until after six hours oxidation is complete. Further, the curves are quite smooth and, as is very well shown in the case of the fatty acids, they are constant and almost coincide over their whole length. The curves also are not identical with that required for a unimolecular reaction, as is shown in Table IV, which gives k_1, the unimolecular constant calculated from the mean experimental curve for linseed oil.

TABLE III.

Data for the Oxidation Curve.

Weight of oil 0·6380 gram. Volume of the apparatus 630 c.c. Temperature 100°. Time period 0·5 hour. Period of induction 20 minutes.

Pressure in mm.	Mean pressure (P_M).	Corrected * time period.	Corrected time.	Percentage absorption.
765	—	0	0	0
737	757	0·494	0·494	3·80
665	701	0·461	0·955	13·58
630	648	0·426	1·381	18·34
610	620	0·408	1·789	21·06
596	603	0·396	2·185	22·96
578	582	0·772	2·957	25·40
572	574	0·377	3·334	26·22
566	569	0·374	3·708	27·04
563	565	0·371	4·079	27·45
560	562	0·369	4·448	27·86
557	559	0·367	4·815	28·26
555	556	0·365	5·180	28·53
553	554	0·364	5·544	28·80
552	553	0·363	5·907	28·90

* Readings were taken every half hour, but owing to the change in oxygen concentration this time period had to be multiplied by $\frac{P_M}{760}$ to obtain a corrected time period which would hold with constant oxygen concentration.

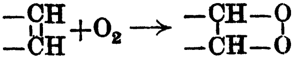
TABLE IV.

Time (t) *	Absorption (x).	$a-x$.	$k_1=\frac{1}{t}\log_e\frac{a}{a-x}$.
0·3	7·4	2·3	0·994
0·7	15·5	13·2	1·110
1·3	20·1	8·6	0·927
1·7	22·7	6·0	0·921
2·3	24·5	4·2	0·836
2·7	25·9	2·8	0·862
3·3	26·9	1·8	0·839
3·7	27·5	1·2	0·858
4·3	28·0	0·7	0·862
4·7	28·4	0·3	0·971
5·3	28·6	0·1	1·068
∞	28·7	—	—

* t is reckoned after the induction period.

Examination of the Volatile Products.

The primary oxidation of linseed oil is probably a molecular autoxidation in which molecules of oxygen are added at the double linkings.



$$\begin{matrix}-\mathrm{CH}\\ \| \\ -\mathrm{CH}\end{matrix} + O_2 \longrightarrow \begin{matrix}-\mathrm{CH}-\mathrm{O}\\ |\qquad | \\ -\mathrm{CH}-\mathrm{O}\end{matrix}$$

The chief evidence in favour of this view is as follows :—

(*a*) In the early stages, the ratio apparent oxygen absorption : decrease in iodine value is approximately $O_2 : I_2$ (Fahrion, *loc. cit.*).

(*b*) During oxidation the linseed oil can liberate iodine from potassium iodide; hence peroxides are formed.

In his extensive researches on autoxidation, Traube (" Vorgänge der Autoxydation," Vieweg, Brunswick, 1904) detected hydrogen peroxide, and therefore it was thought desirable to search for this compound in the volatile products. The oxidation was carried out with a film of oil at 100° in a current of " pure " air. Under these conditions, owing to the elevated temperature, it was probably only possible to detect a small quantity of the hydrogen peroxide produced, but nevertheless a very strong reaction was obtained by passing the volatile products through a starch–potassium iodide solution. From 2 grams of oil iodine equivalent to 0·00136 gram of hydrogen peroxide, or about 0·1 per cent. calculated on the weight of oil used, was obtained. Hydrogen peroxide was also obtained from the fatty acids. It thus seems that the peroxide test might be due in part to hydrogen peroxide and this might be taken as further evidence for assuming this reaction to be an autoxidation.

As mentioned in the introduction, the chief constituents of the volatile products are water, carbon dioxide, and volatile fatty acids, of which acetic acid forms the major part. In order to estimate the proportion of carbon dioxide to fatty acids, therefore, a known amount of oil was put on a filter-paper as usual and oxidised in a stream of oxygen at 100°; the volatile products were passed into a known amount of standard baryta solution. After the reaction the excess of the latter was titrated with standard hydrochloric acid, with phenolphthalein as indicator, and the carbon dioxide in the precipitated barium carbonate was estimated gravimetrically. From these results the amounts of carbon dioxide and of the carboxylic acids given in Table V were calculated.

Ratio $CO_2 : CO_2H = 1 : 1$ for linseed oil.
$= 1 : 0{\cdot}92$ for fatty acids.
$= 1 : 1$ approximately.

TABLE V.

Volatile Acids.

Weight of oil. Grams.	C.c. of $N/10$-$Ba(OH)_2$ neutralised.	Weight of $BaCO_3$. Gram.	Carbon dioxide. Per cent.	Oxygen present as CO_2. Per cent.	Oxygen present as carboxylic acid. Per cent.
2·3900	90·0	0·5763	5·38	3·91	4·25
2·3494	86·3	0·5712	5·41	3·94	3·90
2·3460	86·6	0·5682	5·40	3·94	4·0
2·3500	86·3	0·5721	5·41	3·94	3·92
		Mean	5·40	3·94	3·96
Weight of fatty acids. Gram.					
0·8625	29·8	0·2100	5·5	4·0	3·44
0·9184	33·7	0·2278	5·54	4·03	3·63
	33·0	0·2268	5·52	4·02	3·70
	33·4	0·2270	5·52	4·02	3·67
		Mean	5·[illegible]	4·02	3·67

Discussion of Results and Conclusions.

From the results already given the following conclusions can be drawn.

1. The method used to obtain the oxidation value within a reasonable time is accurate to within 1 per cent.

2. The true oxygen absorption, unlike the apparent oxygen absorption, is a perfectly definite quantity for a given oil (compare Genthe, *loc. cit.*).

3. The ratio of oxygen absorption to iodine absorption is 0·156. This shows that the suggestion of Fahrion (*loc. cit.*) that the ratio is the same as that of the atomic weights, namely, 0·126, is erroneous.

4. From (3) it follows that the oxidation is not simply a molecular autoxidation, because the oxygen absorption is 25 per cent. higher than it would be on this assumption. From Weger's work (see Fahrion, *loc. cit.*) it seems that the primary reaction at least is a molecular autoxidation, and certainly from the fact that atmospheric oxygen is absorbed at the ordinary temperature this seems the most probable course of the reaction. Linseed oil contains 4–5 per cent. of oleic acid, and it is known that this acid does not oxidise at 100°. This corresponds with 4–5 units in the iodine value and therefore the iodine value equivalent to the oxygen absorption is 180 with the oil studied, which on the basis of a simple molecular autoxidation would require an oxygen absorption of 22·7 per cent. This leaves an "*excess*" oxygen absorption of 6·0 per cent. Further, if it is assumed, as a very probable working hypothesis, that the first stage in the oxidation is a molecular

autoxidation, which is followed by a further "*excess*" oxidation giving rise to the volatile acid products, then some relationship might possibly be found between the amount of oxygen in the latter and the "*excess*" oxygen absorption. As already shown, the total amount of oxygen in the volatile acid products is 8 per cent. in the case of linseed oil. Hence the following ratios

$$CO_2 : CO_2H = 1 : 1$$

$$\begin{aligned}\text{Volatile oxygen : excess oxygen} &= 8 : 6\\ &= 4 : 3\\ &= CO_2 + CO_2H : \text{excess oxygen.}\end{aligned}$$

On account of their simplicity, these ratios may be taken as evidence in favour of the above hypothesis.

Linseed oil, however, is a mixture of linolates and linolenates, and as there is no method of satisfactorily estimating these two constituents, the data so far obtained are insufficient to show how each is oxidised and exactly what each contributes to the course of the oxidation of linseed oil. This matter will form the subject of a subsequent communication.

The Effect of the Glyceryl Radicle.

Bauer and Hazura (*Monatsh.*, 1888, **9**, 459) isolated glycerol from linoxyn, and hence it has been assumed that the glyceryl radicle exerts no influence on the course of the reaction.

On this assumption the oxygen absorption calculated from the results obtained with the oil should be 30·00 per cent.; the value actually found by oxidation of the fatty acids is 30·09 per cent.

The calculated quantity of carbon dioxide (5·6 per cent.) agrees closely with that found experimentally with the acids (5·52 per cent.), whilst the $CO_2 : CO_2H$ ratio is in fairly good agreement with that found for linseed oil.

These experimental results, therefore, confirm the suggestion that the glyceryl radicle exerts no influence on the modus operandi of the reactions.

Some investigators have stated that the fatty acids oxidise more slowly than the oil, but it is evident from the curves obtained that the induction period is very small and the rate of oxidation initially much more rapid. This very rapid initial oxidation made it necessary to prepare the acids in an atmosphere of hydrogen. A sample prepared in the ordinary way gave a true oxygen absorption of 28·5 per cent.

The author wishes to express his indebtedness to Professor F. S. Kipping, F.R.S., for his advice and encouragement during this work and to the Department of Scientific and Industrial Research for a grant which enabled him to carry out part of this investigation.

He also wishes to make acknowledgment to the Royal Commissioners for the Exhibition of 1851 for a research scholarship.

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CXXVIII.—*Metallic Derivatives of Nitrophenolic Compounds. Part I. Interaction of Barium, Strontium, and Calcium Hydroxides with the Mononitrophenols.*

By Archibald Edwin Goddard.

These researches are being undertaken, first, to ascertain what influence various metals have on the colour of nitrophenoxides; secondly, to throw further light on the co-ordination numbers of the metals concerned. Finally, it may be possible to ascribe definite formulæ to metallic hydroxides of doubtful composition, on the assumption that each hydroxyl of the latter will react with one phenolic group.

The *o*- and *p*-nitrophenoxides of the above metals were investigated by Fritzsche (*Annalen*, 1859, **110**, 150), but in most cases the only estimation carried out was the water in the hydrated salts, no nitrogen or metal analyses being given. Moreover, neither details of the preparation of the individual hydrates nor their solubilities are recorded.

All the compounds now described were made by the action of the metallic hydroxides on the nitrophenols, but Fritzsche prepared his *para*-compounds by interaction of the chlorides and sodium *p*-nitrophenoxide.

In addition to the already known barium *o*-nitrophenoxide (anhydrous) and the hydrated *para*-salt ($+8H_2O$), the following have been isolated:—*meta*-series, anhydrous salt and hydrated forms containing four and five molecules of water, and the anhydrous *para*-salt.

Post and Mehrtens (*Ber.*, 1875, **8**, 1553) obtained the *meta*-hydrate ($+2H_2O$) as a yellow, crystalline powder, but since its colour does not fall between those of the anhydrous salt and the hydrate ($+4H_2O$), its existence appears to be doubtful.

To the strontium *o*-nitrophenoxide ($+3H_2O$) and *para*-derivative ($+7H_2O$) are now added the anhydrous *ortho*-salt, the corresponding *meta*-compound and its hydrated forms ($+4H_2O$ and $+8H_2O$), and the anhydrous *para*-salt with its hydrate ($+8H_2O$).

In the *meta*-series the hydrate ($+8H_2O$) is unstable in air and rapidly becomes anhydrous, whilst the *para*-compound ($+7H_2O$) has not been again isolated.

In the case of the calcium salts, Fritzsche obtained the hydrated *o*-nitrophenoxides ($+H_2O$ and $+4H_2O$) and mentioned the anhydrous compound; but only one *para*-compound ($+4H_2O$) is described. The author failed to obtain the *ortho*-monohydrate, but isolated the hydrates ($+2H_2O$ and $+4H_2O$). The anhydrous *meta*-derivative and its monohydrate are now described and in the *para*-series the anhydrous compound and hydrated forms ($+2\frac{1}{2}H_2O$, $+3H_2O$, $+5H_2O$, $+8H_2O$).

Details of the preparation of all the above compounds and also of those of Fritzsche are now recorded.

All the *ortho*-salts are red, the *meta*- tend towards orange, and the *para*- yellow, addition of water being coincident with decrease of colour. It would appear that this colour change in the three series is due to the shifting of the nitro-group away from the metal. As the colour decreases the solubility increases, both in anhydrous and hydrated salts. It is noticeable that no *ortho*-derivative has more than four molecules of water, *meta*-salts with more than five molecules seem unstable, but in the *para*-series the maximum is eight and the compounds are quite stable in air.

EXPERIMENTAL.

Barium o-*nitrophenoxide* was obtained by the interaction of 2 grams of barium hydroxide ($8H_2O$) and 1·8 grams of *o*-nitrophenol in 30 c.c. of water, the resulting solution being rapidly concentrated and quickly cooled. Only the anhydrous salt was obtained, which did not melt at 300° (Found : $N=6{\cdot}53$; $Ba=33{\cdot}21$. $C_{12}H_8O_6N_2Ba$ requires $N=6{\cdot}77$; $Ba=33{\cdot}18$ per cent.). The salt crystallises in brilliant scarlet plates which are moderately soluble in warm alcohol, acetone, or pyridine, and insoluble in other organic solvents.

Barium m-*Nitrophenoxides.*—Similar quantities were used to the above and the solution evaporated to about 8 c.c., when orange-yellow needles were obtained (Found: $N=5{\cdot}79$; $Ba=28{\cdot}45$; $H_2O=14{\cdot}95$. $C_{12}H_8O_6N_2Ba,4H_2O$ requires $N=5{\cdot}76$; $Ba=28{\cdot}26$; $H_2O=14{\cdot}82$ per cent.). It is soluble in alcohol, acetone, or pyridine, slightly soluble in chloroform, ethyl acetate, or ether, and insoluble in carbon tetrachloride or toluene, becoming anhydrous in the latter.

In a second preparation, the solution was evaporated to about 15 c.c. and allowed to cool slowly, when long, orange needles were deposited (Found: N=5·55; Ba=27·31; H_2O=17·91. $C_{12}H_8O_6N_2Ba,5H_2O$ requires N=5·56; Ba=27·25; H_2O=17·88 per cent.). In its solubilities this salt is similar to the former one.

By heating either salt at 170—180° for a short time the anhydrous compound was obtained as a dull red powder (Found: N=6·80; Ba=33·45. Calc., N=6·77; Ba=33·18 per cent.). This salt is moderately soluble in ethyl acetate and slightly soluble in ether; its solubility in other solvents is the same as those of its hydrates.

Barium p-*nitrophenoxide* was prepared like the *ortho*-compound (Found: N=6·53; Ba=33·14. Calc. (anhydrous), N=6·77; Ba=33·18 per cent.). The salt crystallises in yellow plates and is soluble in alcohol, acetone, or pyridine and insoluble in other organic solvents. The salt was dissolved in water and allowed to cool very slowly, when large, yellow, rhombic crystals were deposited (Found: Ba=24·34; H_2O=26·14. $C_{12}H_8O_6N_2Ba,8H_2O$ requires Ba=24·61; H_2O=25·82 per cent.).

Strontium o-*nitrophenoxide* was prepared by evaporating a solution containing 2·7 grams of strontium hydroxide ($8H_2O$) and 2·8 grams of *o*-nitrophenol in 50 c.c. of water until crystals appeared (Found: N=6·63; Sr=20·58; H_2O=12·89. $C_{12}H_8O_6N_2Sr,3H_2O$ requires N=6·69; Sr=20·95; H_2O=12·92 per cent.). The salt crystallises in pale orange plates and is readily soluble in cold pyridine, less soluble in warm alcohol, acetone, or ethyl acetate, and insoluble in other solvents. The solutions have a red tone except the one in ethyl acetate, which is bright yellow. In boiling chloroform, the compound becomes deep red, but reverts to its orange colour again on cooling.

By heating the salt at 180° for three hours, the anhydrous, deep orange compound was obtained (Found: N=7·70; Sr=23·70. $C_{12}H_8O_6N_2Sr$ requires N=7·69; Sr=24·05 per cent.). In its solubilities it resembles the hydrate.

Strontium m-*Nitrophenoxides*.—The same quantities were used as in the above case, the solution was evaporated to about 20 c.c. and kept for three days, when long vermilion needles appeared, which were filtered and dried (Found: N=6·40; Sr=19·83; H_2O=15·63. $C_{12}H_8O_6N_2Sr,4H_2O$ requires N=6·42; Sr=20·08; H_2O=16·51 per cent.).

In a second preparation the solution was evaporated to one-third of its bulk and quickly cooled. Golden-orange needles were obtained, which were rapidly dried (Found: N=5·43; Sr=17·23;

$H_2O=28{\cdot}32$. $C_{12}H_8O_6N_2Sr,8H_2O$ requires $N=5{\cdot}52$; $Sr=17{\cdot}24$; $H_2O=28{\cdot}35$ per cent.).

When this compound is exposed to the air for half an hour or left in contact with organic solvents, it becomes anhydrous and brilliant red (Found: $N=7{\cdot}65$, $7{\cdot}70$; $Sr=23{\cdot}84$. Calc., $N=7{\cdot}69$; $Sr=24{\cdot}05$ per cent.). The salt is completely soluble in warm alcohol or acetone (the colour is pure yellow in the latter), moderately soluble in carbon tetrachloride or pyridine, and insoluble in other organic solvents.

Strontium p-*nitrophenoxide*, prepared in the usual way, was allowed to remain for two days before being filtered, and yielded small, brilliant yellow needles (Found: $N=5{\cdot}53$; $Sr=17{\cdot}25$; $H_2O=28{\cdot}14$. Calc. for salt with $8H_2O$, $N=5{\cdot}52$; $Sr=17{\cdot}24$; $H_2O=28{\cdot}35$ per cent.). The salt was soluble in alcohol, acetone, or pyridine, and insoluble in other organic solvents.

Calcium o-*Nitrophenoxides*.—Two grams of *o*-nitrophenol and 0·53 gram of calcium hydroxide were boiled in 50 c.c. of water, the solution was evaporated to 10 c.c. and then cooled. Pale orange, blunt needles were obtained (Found: $N=8{\cdot}03$; $Ca=11{\cdot}55$; $H_2O=10{\cdot}00$. $C_{12}H_8O_6N_2Ca,2H_2O$ requires $N=7{\cdot}94$; $Ca=11{\cdot}36$; $H_2O=10{\cdot}21$ per cent.). The salt is moderately soluble in alcohol, acetone, pyridine, or ethyl acetate, slightly soluble in ether, chloroform, or carbon tetrachloride, and insoluble in toluene or light petroleum.

In a second preparation, when the above quantities were used and the solution was boiled for ten minutes and then cooled, a deposit of pale orange plates was obtained (Found: $N=7{\cdot}25$; $H_2O=18{\cdot}64$. $C_{12}H_8O_6N_2Ca,4H_2O$ requires $N=7{\cdot}21$; $H_2O=18{\cdot}53$ per cent.). By heating this hydrate at 180° for two hours the deep red, anhydrous salt was obtained (Found: $Ca=12{\cdot}65$. Calc., $Ca=12{\cdot}65$ per cent.). This compound differs slightly from the above by being moderately soluble in ether or ethyl acetate, but insoluble in chloroform or carbon tetrachloride.

Calcium m-*Nitrophenoxides*.—When the same quantities were used as for the *ortho*-salt and the solution was boiled for a few minutes, a precipitate of microscopic, reddish-orange needles was obtained (Found: $N=8{\cdot}42$; $Ca=11{\cdot}75$; $H_2O=4{\cdot}96$. $C_{12}H_8O_6N_2Ca,H_2O$ requires $N=8{\cdot}37$; $Ca=11{\cdot}97$; $H_2O=5{\cdot}38$ per cent.).

From a very concentrated aqueous solution of this salt the anhydrous salt is obtained in small rosettes of deep orange needles (Found: $N=9{\cdot}05$; $Ca=12{\cdot}88$. Calc., $N=8{\cdot}85$; $Ca=12{\cdot}65$ per cent.). The anhydrous compound is only slightly soluble in pyridine or chloroform and is insoluble in other organic solvents, but the hydrated salt is soluble in alcohol, ether, pyridine, or chloroform. The anhydrous salt was dissolved in water and the solution kept for several days, when pale orange needles separated, which were found to be a mixture of the above two compounds.

Calcium p-*Nitrophenoxides.*—By heating any of the following hydrated salts at 220° for one hour, the anhydrous compound was obtained as a deep yellow substance (Found: N=8·70; Ca=12·38. Calc., N=8·85; Ca=12·65 per cent.). This salt is soluble in alcohol or pyridine, slightly soluble in ether, and insoluble in other organic solvents.

By the use of the same quantities as in the preparation of the *ortho*-salt, evaporation to 30 c.c. and keeping overnight, long, lemon-yellow needles separated (Found: N=6·93; Ca=9·64; H_2O=21·62. $C_{12}H_8O_6N_2Ca,5H_2O$ requires N=6·89; Ca=9·85; H_2O=22·14 per cent.). This hydrate is soluble in acetone, but insoluble in ether.

In a second preparation a solution of 4 grams of the nitrophenol and 1·06 grams of calcium hydroxide in 60 c.c. of water was boiled and filtered. Short, microscopic, yellow needles separated and were rapidly dried (Found: N=7·90; Ca=11·07; H_2O=12·56. $C_{12}H_8O_6N_2Ca,2\frac{1}{2}H_2O$ requires N=7·75; Ca=11·08; H_2O=12·45 per cent.).

The filtrate from these crystals was evaporated to 10 c.c. and slowly cooled. Glistening yellow needles were deposited (Found: Ca=8·38; H_2O=31·24. $C_{12}H_8O_6N_2Ca,8H_2O$ requires Ca=8·69; H_2O=31·27 per cent.). This salt differs from the hydrate ($+5H_2O$) in being soluble in ether, and it melts in its own water of crystallisation at 80—90°. From the above hydrate ($+2\frac{1}{2}H_2O$), by exposure to air, the hydrate ($+3H_2O$) was obtained (Found: N=7·68; Ca=10·85; H_2O=14·70. Calc., N=7·56; Ca=10·81; H_2O=14·58 per cent.).

The author desires to express his thanks to Professor G. T. Morgan for the interest he has shown in this work.

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CXXIX.—*Interaction of Sulphur Monochloride and Organic Acid Amides.*

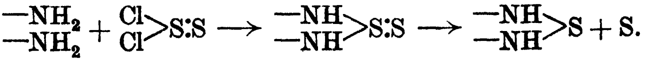
By KUVERJI GOSAI NAIK.

THE reaction of acid chlorides with amides, amines, and their derivatives appears to have been extensively studied. In particular, a number of investigations on the interaction of various amines and sulphur monochloride have been carried out (Claus and Krall, *Ber.*, 1871, **4**, 99; Edeleano, *Bull. Soc. chim.*, 1891, [iii], **5**, 173; Roorda Smit, *Ber.*, 1875, **8**, 1445; Schmidt, *Ber.*, 1878, **11**, 1168; Michaelis, *Ber.*, 1895, **28**, 165), but no systematic study of the interaction of sulphur monochloride and organic acid amides or their substituted derivatives appears to have been made.

The reaction of sulphur monochloride with dry ammonia gas is very vigorous. When sulphur monochloride is dropped into the gas, flashes of light are produced and heavy clouds of ammonium chloride are developed, with the simultaneous deposition of sulphur.

In view of this it is to be expected that—

(i) The amido-group in the organic amides will readily react with sulphur monochloride and give rise to sulphides:



$$\begin{matrix}-NH_2\\-NH_2\end{matrix} + \begin{matrix}Cl\\Cl\end{matrix}\!>\!S{:}S \longrightarrow \begin{matrix}-NH\\-NH\end{matrix}\!>\!S{:}S \longrightarrow \begin{matrix}-NH\\-NH\end{matrix}\!>\!S + S.$$

(ii) Amines will be more reactive than amides on account of their more strongly basic character.

(iii) Amides of the monocarboxylic acids, such as acetamide, may be expected to condense with sulphur monochloride more readily than the amides of the dicarboxylic acids, such as oxamide, because the two carbamyl groups in adjacent positions in the latter may be expected to increase the acidity, and thus render the NH_2-group in such amides less reactive.

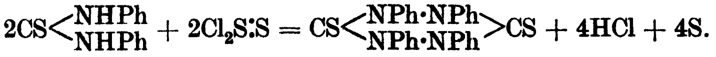
These expectations have been fulfilled by the results of the present work. Oxamide, succinamide, malonamide, phthalamide, and phthalimide do not react with sulphur monochloride. Oxanilide also proved unreactive, whilst malonanilide condensed in the manner characteristic of $\cdot CO \cdot CH_2 \cdot CO \cdot$ derivatives (this vol., p. 379).

As regards the other amides which have been investigated, namely, acetamide, butyramide, benzamide, benzanilide, carbamide, thiocarbamide, thiocarbanilide, and salicylamide, it may be noted in the first place that carbamide gave chiefly ammonium chloride and sulphur, along with hydrogen chloride. The reactions with acetamide, butyramide, and benzamide followed a very simple course, two molecules of the amide condensing with one molecule of sulphur monochloride to give a diamido-sulphide. Thus:

$$2CH_3\cdot CO\cdot NH_2 + Cl_2S{:}S = (CH_3\cdot CO\cdot NH)_2S + 2HCl + S.$$

(I.)

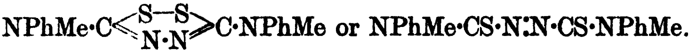
The reaction with thiocarbanilide resulted in the condensation of two molecules of the anilide:



$$2CS{<}^{NHPh}_{NHPh} + 2Cl_2S{:}S = CS{<}^{NPh\cdot NPh}_{NPh\cdot NPh}{>}CS + 4HCl + 4S.$$

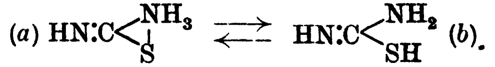
(II.)

This reaction is similar in many respects to that observed by Hector (*J. pr. Chem.*, 1892, [ii], **44**, 492; compare also Dodt, *Ber.*, 1906, **39**, 1014), who found that two molecules of an unsymmetrical disubstituted thiocarbamide condense under the influence of sulphur monochloride, giving a product from which the four hydrogen atoms have been eliminated,



$$NPhMe\cdot C{<}^{S-S}_{N\cdot N}{>}C\cdot NPhMe \text{ or } NPhMe\cdot CS\cdot N{:}N\cdot CS\cdot NPhMe.$$

The reaction with thiocarbamide is specially interesting, as it can be explained on Werner's view of the constitution of thiocarbamide. Werner (T., 1919, **115**, 1168) suggested that in a neutral solution thiocarbamide is present in two forms in equilibrium, thus:



$$(a)\ HN{:}C{<}^{NH_3}_{\underset{S}{|}} \rightleftharpoons HN{:}C{<}^{NH_2}_{SH}\ (b).$$

In the present case, the form (*b*) can be taken as the active modification, the reaction with sulphur monochloride being as follows:

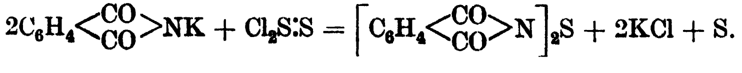
$$2NH{:}C(NH_2)\cdot SH + Cl_2S{:}S = [NH{:}C(NH_2)\cdot S]_2S,2HCl + S.$$

(III.)

Benzanilide reacts with sulphur monochloride to produce a trisulphide, $S(S\cdot C_6H_4\cdot NH\cdot COPh)_2$, similar to that resulting from acetanilide and sulphur monochloride (Schmidt, *loc. cit.*), whilst salicylamide produces a disulphide,

$$NH_2\cdot CO\cdot C_6H_3(OH)\cdot S\cdot S\cdot C_6H_3(OH)\cdot CO\cdot NH_2.$$

Although phthalimide has no action on sulphur monochloride, its potassium derivative reacts to form a di-imino-sulphide,



$$2C_6H_4{<}^{CO}_{CO}{>}NK + Cl_2S{:}S = \left[C_6H_4{<}^{CO}_{CO}{>}N\right]_2S + 2KCl + S.$$

EXPERIMENTAL.

N-*Sulphidobisacetamide* (I).

Sulphur monochloride (25 grams), dissolved in a small quantity of benzene, was gradually added to a boiling solution of acetamide

(10 grams) in dry benzene (200 c.c.). The reaction began at once, with the slow evolution of hydrogen chloride. After six hours, the undissolved white mass was collected, washed with dry benzene to remove the undecomposed sulphur monochloride, and crystallised from alcohol, from which the product separated in slender needles, m. p. 192°.

The compound dissolved readily in hot water, and decomposed aqueous silver nitrate with the formation of silver sulphide. A solution in sodium carbonate, on boiling and then acidifying, evolved hydrogen sulphide (Found: $S=21{\cdot}48$; $N=19{\cdot}27$. $C_4H_8O_2N_2S$ requires $S=21{\cdot}62$; $N=18{\cdot}92$ per cent.).

N-*Sulphidobisbenzamide*, $(C_6H_5{\cdot}CO{\cdot}NH)_2S$.

This substance was prepared from benzamide (10 grams) and sulphur monochloride (11 grams) in the same way as the preceding sulphide. The white, amorphous solid was sparingly soluble in benzene, from which it crystallised in fibrous needles melting at 188°. The product was insoluble in water and reacted neither with sodium carbonate solution nor with silver nitrate (Found : $S=11{\cdot}90$; $N=10{\cdot}14$. $C_{14}H_{12}O_2N_2S$ requires $S=11{\cdot}76$; $N=10{\cdot}29$ per cent.).

N-*Sulphidobisbutyramide*, $(C_3H_7{\cdot}CO{\cdot}NH)_2S$.

This substance, prepared from butyramide (5 grams) and sulphur monochloride (5 grams), in presence of dry benzene (50 c.c.) in the same way as the sulphidobisacetamide, was deposited as a solid very sparingly soluble in benzene, from which it separated in minute white crystals melting sharply at 175° (Found : $N=13{\cdot}41$; $S=16{\cdot}05$. $C_8H_{16}O_2N_2S$ requires $N=13{\cdot}72$; $S=15{\cdot}68$ per cent.).

Sulphidodithiocarbamide Dihydrochloride (III).

Sulphur monochloride (7 grams) was slowly run into a boiling solution of thiocarbamide (9 grams) in absolute alcohol (100 grams) previously saturated with sulphur monochloride. When the vigorous reaction had abated, the mixture was boiled for three hours and the hard yellow mass collected and extracted with a large quantity of alcohol and carbon disulphide until no more sulphur was removed. The resulting, pale yellow substance was insoluble in chloroform, ethylene dichloride, benzene, light petroleum, acetic acid, carbon tetrachloride, or nitrobenzene, and melted with decomposition at 176—177°. On keeping under water it slowly deposited sulphur, hydrochloric acid being simultaneously formed. On treatment with sodium carbonate carbon dioxide was evolved. Sodium hydroxide first precipitated sulphur, which then dissolved in excess of the boiling alkali, from which, on acidification, hydrogen sulphide was evolved. On treating the aqueous solution with silver nitrate, silver chloride was at once precipitated, but it immediately darkened on the addition of concentrated ammonia owing to the formation of silver sulphide (Found: S=37·12; Cl=28·30; N=22·00. $C_2H_6N_4S_3,2HCl$ requires S=37·63; Cl=28·62; N=21·96 per cent.).

3 : 6-*Dithio*-1 : 2 : 4 : 5-*tetraphenylhexahydro*-1 : 2 : 4 : 5-*tetrazine* (II).

A mixture of thiocarbanilide (8 grams), sulphur monochloride (5 grams), and dry benzene (200 c.c.) was boiled for three hours, when the solid was collected and washed repeatedly with dry benzene to remove any excess of sulphur monochloride. The substance was then dissolved in benzene, the solution treated with reduced copper until the free sulphur had been eliminated, and evaporated until prismatic crystals, melting sharply at 160°, were deposited. The mixture with thiocarbanilide melted at 138°.

The tetrazine is stable and is not affected by water, in which it is insoluble (Found: C=68·39; H=4·50; N=12·90; S=14·67. $C_{26}H_{20}N_4S_2$ requires C=69·02; H=4·42; N=12·39; S=14·15 per cent.).

Trisulphidobisbenzanilide, $S(S{\cdot}C_6H_4{\cdot}NH{\cdot}COPh)_2$.

Reaction quickly set in when benzanilide (14 grams) was heated with sulphur monochloride (10 grams). The dark brown solid formed was washed with dry petroleum and then precipitated from an alcoholic solution by means of water. The yellowish-white precipitate was purified in benzene solution by reduced copper as in the last experiment, and was obtained as a flocculent precipitate, m. p. 244° (Found: N=5·98; S=20·17. $C_{26}H_{20}O_2N_2S_3$ requires N=5·74; S=19·67 per cent.).

Disulphidobis-salicylamide, $S_2[C_6H_3(OH){\cdot}CO{\cdot}NH_2]_2$.

A mixture of 5 grams of salicylamide, 50 c.c. of dry benzene, and 5 grams of sulphur monochloride was heated under reflux for three hours. The product was washed with dry benzene and caused to separate several times from methyl alcohol by spontaneous evaporation. It was thus obtained as a yellow, amorphous solid which melted and decomposed at 226° (Found: S=18·51. $C_{14}H_{12}O_4N_2S_2$ requires S=19·04 per cent.).

N-*Sulphidodiphthalimide*, $\left[C_6H_4{<}^{CO}_{CO}{>}N\right]_2S$.

The dried potassium salt (compare Landsberg, *Annalen*, 1882, **215**, 181) of phthalimide (two mols.) and sulphur monochloride (one mol.) were heated with dry light petroleum under reflux for one hour. The residue was repeatedly extracted with dry light petroleum and finally purified by treatment with reduced copper in benzene as in the previous cases. The compound was thus obtained as white crystals which melted at 190°, and decomposed on keeping (Found: N=8·41; S—9·64. $C_{16}H_8O_4N_2S$ requires N=8·64; S=9·87 per cent.).

In conclusion, I have very great pleasure in recording my thanks to Prof. J. F. Thorpe and Dr. M. A. Whiteley for their keen interest and kind encouragement throughout the progress of this work, and to the Chemical Society for a grant from their Research Fund which has partly defrayed the expenses incurred in this investigation.

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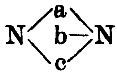
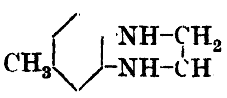
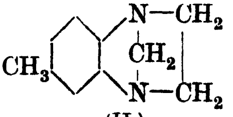
CXXX.—*Some New Tricyclic Bases.*

By TOM SIDNEY MOORE and IDA DOUBLEDAY.

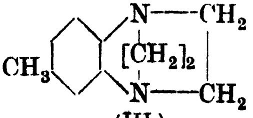
IN a preliminary note on asymmetric tervalent nitrogen (Moore, P., 1914, **30**, 182) attention was directed to the importance of examining substances of the type , where a, b, and c are three different groups or chains, of which at least one is unsymmetrical with regard to the two nitrogen atoms. Three compounds, II, III, and IV, of this type have been prepared and are here shortly described.



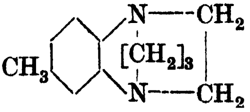
(I.)



(II.)



(III.)



(IV.)

1 : 4-*endo*Methylene-6-methyltetrahydroquinoxaline (II) is prepared from 6-methyltetrahydroquinoxaline (I) by treatment with formaldehyde or, better, by treatment with methylene iodide (84 per cent. yield). The 1 : 4-*endo*ethylene- and 1 : 4-*endo*trimethylene-compounds (III) and (IV) are prepared by similar treatment of I, with ethylene dibromide and trimethylene dibromide, but under similar conditions smaller yields of the new bases are obtained as the carbon chain introduced lengthens.

These compounds are white, microcrystalline solids, melting with decomposition. They dissolve in glacial acetic acid to give red solutions, in which they have molecular weights corresponding with the formulæ given, but in benzene and nitrobenzene they dissolve without changing the colour of the solvent, and in these solutions are bimolecular. They are insoluble in aqueous alkalis and dissolve in dilute mineral acids to give red solutions.

Derivatives containing one and two molecules of hydrochloric acid, oxalic acid, and of methyl iodide to one molecule of base have been prepared from compound II, and similar hydrochloric and oxalic acid derivatives from compounds III and IV. The colours of the derivatives of compound II—(III and IV give exactly similar results)—are shown in the following table :

Compound.	Colour of the solid.	Colour of the solution.	Mol. wt. Found.	Mol. wt. Calc^{d}.
$C_{10}H_{12}N_2$ (II)	White	Colourless in benzene	312	160
,,		,, in nitrobenzene	316	,,
,,		Red in acetic acid	163	,,
$C_{10}H_{12}N_2,HCl$	White	Colourless in water	—	
$C_{10}H_{12}N_2,2HCl$	Reddish-brown	Reddish-brown in water	—	
$C_{10}H_{12}N_2,H_2C_2O_4$	,, ,,	,, ,, ,, ,,	—	
		Red in acetic acid	—	
		,, ,, phenol	238	250
$C_{10}H_{12}N_2,2H_2C_2O_4$	Yellowish-brown	Purplish-red in water	—	
		,, ,, ,, alcohol	—	
		Reddish-brown in acetic acid	—	
		Red in phenol	351	340
$C_{10}H_{12}N_2,CH_3I$	Reddish-brown	Reddish-brown in water	—	
		Red in phenol	297	302
$C_{10}H_{12}N_2,2CH_3I$	Yellowish-brown	Reddish-brown in water	—	
		Greenish-brown in alcohol	—	
		Red in phenol	415	444

These results are unexpected if the substances are taken to have the formulæ given and if no structural change other than the formation of quinquevalent nitrogen takes place on salt-formation. On the other hand, it is not easy to conceive any probable constitutional change that would lead to formulæ for the saturated compounds from which colour could be predicted. No proof of structure is put forward in this paper, but as regards the bases themselves the method of formation leads directly to the formulæ given, and they give derivatives having the expected empirical formulæ and molecular weights. Before the colour observations and the constitution of the derivatives can be discussed with advantage it is necessary to examine other compounds of the same type—some purely aliphatic—and no discussion is here attempted. The purpose of this paper is to record the results so far obtained, and to establish a claim to this field of work.

EXPERIMENTAL.

1 : 4-endo*Methylene-6-methyltetrahydroquinoxaline* (II) *and its Derivatives.*

The base was prepared by heating 6-methyltetrahydroquinoxaline with a little water and the equivalent quantity of paraformaldehyde at 120° for two hours. The product was boiled with water to extract any unchanged parent-substance, and the residue, after drying, extracted with cold benzene. By addition of light petroleum to the benzene solution, filtration of the white, flocculent precipitate which was formed, and slow evaporation of the solution, a faintly brown, apparently amorphous, substance was obtained. A second similar treatment both of the original residue and of the substance first precipitated by light petroleum yielded further quantities of this substance, which was best purified by repetition of the whole process, until a product easily and completely soluble in cold benzene was obtained (Found: C=75·20; H=7·35; N=17·39. M=163, 158 [in glacial acetic acid], 357, 355 [in benzene], 296, 310 [in nitrobenzene]. $C_{10}H_{12}N_2$ requires C=75·00; H=7·50; N=17·50 per cent. M=160).

The compound is white with a faint brown tinge, and melts with decomposition at 150°. It dissolves readily in benzene and nitrobenzene (colourless solutions) and in glacial acetic acid and dilute mineral acids (red colour). It is insoluble in aqueous alkalis and in the majority of organic solvents.

The same compound was also prepared by heating 6-methyltetrahydroquinoxaline with the equivalent quantity of methylene iodide at 100° for four hours. The dark red, crystalline solid formed was dissolved in water, the solution treated with animal charcoal, and the base precipitated by the addition of sodium hydroxide. Purification was effected by precipitation from benzene solution with light petroleum, but much less matter insoluble in benzene was present than in the first method of preparation, and the final yield was 84 per cent. of the theoretical (Found: C=74·80; H=7·43; N=17·42 per cent. M=165 [in acetic acid], 312, 316 [in benzene]).

The *monohydrochloride* was prepared by passing dry hydrogen chloride into the benzene solution of the base, and allowing the white precipitate which separated to remain in a vacuum in presence of solid sodium hydroxide for several weeks (Found: $Cl=17{\cdot}84$. $C_{10}H_{12}N_2,HCl$ requires $Cl=18{\cdot}06$ per cent.).

The *dihydrochloride* was prepared by continuing the passage of hydrogen chloride until the white monohydrochloride, formed as described above, was completely changed to a reddish-brown, viscous, partly crystalline mass. This was filtered off, washed with dry benzene, and transferred to a vacuum desiccator as quickly as possible, on account of its extremely hygroscopic character (Found: $Cl=30{\cdot}16$. $C_{10}H_{12}N_2,2HCl$ requires $Cl=30{\cdot}47$ per cent.).

Both hydrochlorides are readily soluble in water, the monohydrochloride giving a colourless solution and the dihydrochloride dissolving to give a reddish-brown solution. The base is recovered unchanged on addition of sodium hydroxide.

The *normal oxalate* was obtained by adding the calculated quantity of oxalic acid dissolved in alcohol to the base dissolved in benzene, and warming. A reddish-brown, viscous substance separated, which hardened on cooling. After extraction with warm alcohol and warm benzene, it was analysed (Found: $C=57{\cdot}35$; $H=5{\cdot}51$. $M=238$ [in phenol]. $C_{10}H_{12}N_2,H_2C_2O_4$ requires $C=57{\cdot}60$; $H=5{\cdot}60$ per cent. $M=250$).

This compound is a reddish-brown, hygroscopic solid, which dissolves in water, glacial acetic acid, and phenol to give red solutions. It is slightly soluble in alcohol and almost insoluble in other organic solvents.

The *acid oxalate* proved difficult to prepare, but was finally obtained by the slow addition of the finely powdered base to the calculated quantity of oxalic acid dissolved in hot alcohol. The base dissolved, giving a purplish-red solution, which on evaporation in a vacuum gave the acid oxalate as a yellowish-brown, extremely hygroscopic solid, which dissolved in water and alcohol to give purplish-red solutions, in glacial acetic acid to a reddish-brown solution, and was slightly soluble in benzene and chloroform to give reddish-brown solutions (Found: $C=49{\cdot}32$; $H=4{\cdot}79$. $M=351$ [in phenol]. $C_{10}H_{12}N_2,2H_2C_2O_4$ requires $C=49{\cdot}41$; $H=4{\cdot}70$ per cent. $M=340$).

The *monomethiodide* was prepared by boiling the base with excess of methyl iodide for three hours. On cooling, the methiodide crystallised out and was purified by recrystallisation from moist acetone (Found: $I=42{\cdot}12$. $M=297$ [in phenol]. $C_{10}H_{12}N_2,MeI$ requires $I=42{\cdot}05$ per cent. $M=302$).

The compound is a reddish-brown, crystalline powder easily soluble in phenol (red solution), moderately soluble in water (reddish-brown solution), sparingly soluble in dry acetone or alcohol, and insoluble in benzene, light petroleum, or chloroform. It melts with decomposition at 118—120°.

The same compound may be prepared in the cold by slow addition of the base to excess of methyl iodide dissolved in alcohol. On keeping, the methiodide crystallises out (Found: $I=41\cdot93$ per cent.).

The *dimethiodide* was prepared by heating the base with excess of methyl iodide for six hours at 130°. A viscous solid was produced, which was analysed after recrystallisation from moist acetone (Found: $I=57\cdot41$. $M=415$ [in phenol]. $C_{10}H_{12}N_2,2MeI$ requires $I=57\cdot20$ per cent. $M=444$).

This compound is a yellowish-brown, extremely hygroscopic, crystalline solid, melting with decomposition at 101°. It is easily soluble in water (reddish-brown solution), ethyl alcohol (greenish-brown solution) and in phenol (red solution), less soluble in dry acetone, and insoluble in benzene or chloroform.

1 : 4-endo*Ethylene-6-methyltetrahydroquinoxaline* (III), 1 : 4-endo*Trimethylene-6-methyltetrahydroquinoxaline* (IV), *and their Derivatives.*

These compounds were prepared by exactly similar methods and showed similar properties to the compounds above described. The analyses and molecular-weight determinations gave the following results:

1 : 4-endo*Ethylene-6-methyltetrahydroquinoxaline* melts at 175° with decomposition (Found: $C=75\cdot78$; $H=8\cdot01$; $N=16\cdot02$. $M=168$, 177 [in acetic acid]. $C_{11}H_{14}N_2$ requires $C=75\cdot86$; $H=8\cdot04$; $N=16\cdot09$ per cent. $M=174$).

Monohydrochloride (Found: $Cl=16\cdot12$. $C_{11}H_{14}N_2,HCl$ requires $Cl=16\cdot38$ per cent.).

Dihydrochloride (Found: $Cl=28\cdot58$. $C_{11}H_{14}N_2,2HCl$ requires $Cl=28\cdot73$ per cent.).

Normal oxalate (Found: $C=59\cdot21$; $H=6\cdot13$. $C_{11}H_{14}N_2,H_2C_2O_4$ requires $C=59\cdot09$; $H=6\cdot06$ per cent.).

Acid oxalate (Found: $C=50\cdot95$; $H=5\cdot05$. $C_{11}H_{14}N_2,2H_2C_2O_4$ requires $C=50\cdot86$; $H=5\cdot09$ per cent.).

1 : 4-endo*Trimethylene-6-methyltetrahydroquinoxaline* melts at 192° with decomposition (Found: $C=76\cdot60$; $H=8\cdot49$; $N=14\cdot89$. $M=181$ [in acetic acid]. $C_{12}H_{16}N_2$ requires $C=76\cdot58$; $H=8\cdot51$; $N=14\cdot90$ per cent. $M=188$).

Monohydrochloride (Found: $Cl=15\cdot68$. $C_{12}H_{16}N_2,HCl$ requires $Cl=15\cdot81$ per cent.).

Dihydrochloride (Found: Cl=27·43. $C_{12}H_{16}N_2,2HCl$ requires Cl=27·20 per cent.).

Normal oxalate (Found: C=60·38; H=6·52. $C_{12}H_{16}N_2,H_2C_2O_4$ requires C=60·43; H=6·48 per cent.).

Acid oxalate (Found: C=52·27; H=5·45. $C_{12}H_{16}N_2,2H_2C_2O_4$ requires C=52·18; H=5·44 per cent.).

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ROYAL HOLLOWAY COLLEGE. [*Received, May 25th,* 1921.]

CXXXI.—*The Structural Isomerism of the Oximes. Part I. Criticism of the Hantzsch-Werner Hypothesis and a New Theory of the Constitution of Isomeric Oximes.*

By FREDERICK WILLIAM ATACK.

FUNDAMENTAL differences have been shown to exist in the salt-forming properties of the oxime groups present in the three benzildioximes (Atack, T., 1913, **103**, 1317), and it has since been noted that of the two benzilmonoximes, only the α-isomeride forms a nickel salt. Similar differences have been noted by Whiteley (T., 1903, **83**, 24) in the reaction of the benzildioximes with ferrous salts. Beck and Hase (*Annalen*, 1907, **355**, 29) found that an alcoholic solution of β-benzaldoxime ("*syn*"), but not that of α-benzaldoxime ("*anti*"), gives a blood-red coloration with ferric chloride and an olive-green coloration with copper acetate. No explanation of these differences is possible if the Hantzsch-Werner hypothesis of the stereochemical isomerism of the oximes is adopted.

In an attempt to estimate α-benzildioxime volumetrically by the method used for the β-isomeride (Atack, *loc. cit.*, p. 1319), irregular results were obtained unless the α-dioxime had first been converted into the β-isomeride, as the α-dioxime required a larger amount of the reducing agent. The reduction products are being further investigated, but the difference in behaviour is considered to prove that the two isomerides are not structurally identical, as has been assumed in the Hantzsch-Werner hypothesis. Brady and Dunn (T., 1916, **109**, 655) satisfactorily disposed of Goldschmidt's supposed proof (*Ber.*, 1889, **22**, 3113) of the structural identity of isomeric oximes by showing that phenylcarbimide gives identical compounds from both the *syn-* and *anti*-benzaldoximes.

The Beckmann reaction has been used for determining the configuration of the ketoximes according to the Hantzsch-Werner hypothesis. The present author directed attention (*Proc. Manc. Lit. and Phil. Soc.*, Nov. 17th, 1914) to the fact that a discrepancy which has never been explained exists between the formulæ first adopted by Hantzsch and Werner based on the properties of the isomeric benzildioximes and the formulæ they later accepted based on the Beckmann reaction.

As will be shown in the subsequent communication, a fourth benzildioxime may readily be obtained, whereas the Hantzsch-Werner hypothesis only admits the possible existence of three isomerides.

The evidence in favour of the Hantzsch-Werner hypothesis for explaining the isomerism of oximes appears overwhelming as outlined in their two publications (Hantzsch, "Grundriss der Stereochemie," 1904, 2nd edition; Werner, "Lehrbuch der Stereochemie," 1904), but in view of the above facts, the question arises whether this hypothesis is really necessary to explain the existence of isomeric oximes, or whether this could not be explained satisfactorily by the presence of groups of different structure.

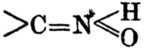
The Hantzsch-Werner hypothesis has not been without critics. The assumption on which the hypothesis is based is the distribution of the valency directions of tervalent nitrogen along the edges of a tetrahedron, at the apex of which the nitrogen atom is supposed to be situated. Criticism has been directed mainly towards the reason why such an unsymmetrical arrangement of the valency directions can attain the rigidity demanded by the permanent existence of definite compounds having characteristic properties. Pickering (T., 1893, **63**, 1070) remarks: "As the nitrogen atom does not combine with as many as the four hydrogen atoms which are required to form the four corners of a tetrahedron, this figure can only be obtained by taking the nitrogen atom out of the centre of the tetrahedron and making it do duty for one of the corners itself. The atoms are thus no longer arranged about the one with which they are united, but are all grouped on one side of it, the other side being apparently paralysed and incapable of combination." Moreover, all attempts to prepare stereoisomeric substituted amines have failed.

The chemical properties of the oxime group have not been the subject of many investigations. Research has been directed more towards the existence or otherwise of isomerides and the relative stability of the *syn-* and *anti*-modifications than to the chemical behaviour of the oxime groups, and in particular the exact nature of the formation of salts by oximes.

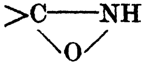
Hantzsch (" Grundriss," p. 130) has found it necessary to assume a different charge (+ or —) on the *syn*- and *anti*-groups respectively to account for the different stability of oximes, and states definitely that all oximes exist in one configuration stable to alkalis (as the sodium compound), and in the other configuration stable to acids (as the hydrochloride or acetyl derivative). If this statement were true, it would in itself vitiate the Hantzsch-Werner stereochemical hypothesis, as such characteristic behaviour must be due to *structural* isomerism.

It has been found that a complete explanation of the existence and behaviour of isomeric oximes may be based on structural formulæ. The new theory depends essentially on the existence of a generally unstable modification (formula II), containing quinquevalent nitrogen, intermediate between the two usually stable isomerides (formulæ I and III) containing tervalent nitrogen. Compounds having such formulæ might be expected to have different salt-forming properties.

(I) $>C=N-O-H$ " oxime "

(II) 

$>C=N{<}^{H}_{O}$ " nitrone "

(III)  " *iso*oxime "

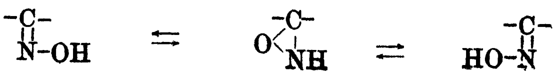
A substance containing a group of formula (II) would probably be difficult to isolate, although its alkyl compound would be more stable. Such alkyl compounds are described by Staudinger and Miescher (*Helv. Chim. Acta,* 1919, **2**, 554), who proved their constitution from the nature of the additive product formed with diphenylketen. The *N*-ethers of the oximes are called " nitrones " by these authors, although Pfeiffer (*Annalen,* 1916, **411**, 72) first applied the term in rather a different manner, in connexion with his preparation of a *N*-oxime (that is, $>$N:NOH) from a " nitrone," for example, from 2-phenylisatogen (in addition to the normal *C*-oxime given by this substance). The name " nitrone " has therefore been adopted for the group of formula (II).

There are therefore two structural formulæ (I) and (III) which would represent groups of sufficient stability to enable compounds containing them to be isolated in the free state. The number of isomerides which it would generally be possible to isolate will therefore be identical with the number predicted by the Hantzsch-Werner hypothesis.

It would, however, be expected that in suitable circumstances there would be a possibility of isolating the third isomeric oxime having the " nitrone " formula (II). It is of interest to note that Beckmann (*Ber.*, 1904, **37**, 3042) has prepared a third modification of benzaldoxime, but refers to it as a " monotropic " modification of benz*anti*aldoxime. The properties of the third modification are being further investigated.

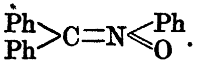
In the case of the methylbenzhydroximic acids, two isomerides of m. p. 64° and 44° are described by Werner and Subak (*Ber.*, 1896, **29**, 1153). The third isomeride of m. p. 101° had been prepared by Lossen (*Annalen*, 1894, **281**, 199) by the same method previously used by Lossen and Zanni for the preparation of the isomeride of m. p. 64°, no reason being available to account for the different product obtained in the later experiments. Werner (*Ber.*, 1896, **29**, 1150) obtained the isomeride of m. p. 101° by recrystallising the modification of m. p. 64° in the neighbourhood of a recrystallisation of the compound of m. p. 101°, whereas recrystallisation of the modification of m. p. 64° in another room gave the original substance of m. p. 64°. He obtained identical derivatives from the two modifications and remarks : " Mann muss somit annehmen, das eine Art physikalischer Isomerie vorliegt, wobei mir die Annahme einer auf den festen Zustand beschränkten Polymerie die einfachste Erklärung für die Thatsachen zu bieten scheint." It is not clear why Werner arrived at the conclusion that the isomerism only exists in the solid state, in view of the fact that both compounds could be recrystallised from the same solvent.

Formula (III) was adopted by Beckmann (*Ber.*, 1890, **23**, 3335) for benz*syn*aldoxime. Supporters of the " *iso*oxime " formula (III) still exist in spite of the Hantzsch-Werner hypothesis. Thus Beck and Hase (*loc. cit.*, p. 54) adopt this formula for benz*syn*aldoxime in view of the characteristic colour reactions given only by this isomeride. Scheiber (*Ber.*, 1911, **44**, 761) failed to obtain optically active modifications of *syn*-aldoximes such as are called for by the " *iso*oxime " structure, but his results may be explained by the fact that his researches were carried out with the stable *N*-alkylated oximes, now known to have the " nitrone " structure, which does not contain an asymmetric carbon atom. Mills and Bain (T., 1910, **97**, 1870) consider that the evanescent character of the activity of the *d*- and *l*- modifications of the oxime of *cyclo*hexanone-4-carboxylic acid is determined in some manner by the presence of the >C:NOH group, and later (p. 1882) suggest that the conversion may take place through an " *iso*oximino-form " :



The results of Mills and Bain have generally been interpreted as final evidence in favour of the Hantzsch-Werner hypothesis, but they only appear to prove that the nitrogen valencies are not coplanar. It is quite conceivable that the active oxime was the "nitrone" form, containing quinquevalent nitrogen, in which the valencies would certainly not be coplanar, and this would lead to a "centroasymmetric" molecule (Perkin and Pope, T., 1911, **99**, 1512). The formation of a "nitrone" would be essential as an intermediate stage between the "*iso*oxime" and "oxime" formulæ represented above. It is to be noted that these authors found (*loc. cit.*, p. 1869) that, contrary to the general rule, alkali retarded racemisation, whereas the activity disappeared on acidifying, which would convert the active "nitrone" oxime into the inactive "oxime" isomeride.

Symmetrical ketoximes are only known to exist in one modification. The stable character of symmetrical compounds is well recognised, and the most symmetrical compound would contain the $>C{=}N{-}OH$ group. Derivatives of the symmetrical ketoximes are known which have isomeric formulæ. Thus Staudinger and Miescher (*Helv. Chim. Acta*, 1919, **2**, 562) assign to diphenyl-*N*-phenyl nitrone (*N*-phenyl ether of benzophenoneoxime) the formula:

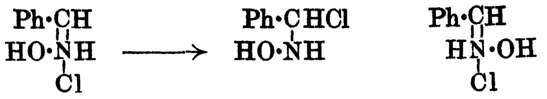


$$\begin{matrix}Ph\\Ph\end{matrix}\!>C{=}N\!<\!\begin{matrix}Ph\\O\end{matrix}.$$

Semper and Lichtenstadt (*Ber.*, 1918, **51**, 933) have prepared both the *N*-methyl and *O*-methyl ether of benzophenoneoxime by direct methylation.

Interconversion of the Isomeric Oximes.

The facility of interconversion of the isomeric oximes has been considered to support the Hantzsch-Werner hypothesis, but it must be remarked that neither Hantzsch nor Werner has offered any explanation whatever of the fact that only the *anti*-oxime is stable to dilute acids, or why this oxime is, on the other hand, converted into the isomeric *syn*-oxime (unstable to dilute acids) by dry hydrogen chloride. Brady and Dunn (T., 1916, **109**, 663) advance the explanation that the latter occurs by the addition of the hydrogen chloride taking place at both double bonds, with subsequent elimination, by means of sodium carbonate, of a different hydrogen atom from that originally combined with chlorine, "and consequently the relative positions of the groups are altered with the formation of the *syn*-oxime," to the three hydrochlorides being assigned (*loc. cit.*, pp. 658, 663) the formulæ:



$$\begin{array}{c}\mathrm{Ph{\cdot}CH}\\ \|\\ \mathrm{HO{\cdot}NH}\\ |\\ \mathrm{Cl}\end{array} \longrightarrow \begin{array}{c}\mathrm{Ph{\cdot}CHCl}\\ |\\ \mathrm{HO{\cdot}NH}\\ \\ \\ \end{array} \qquad \begin{array}{c}\mathrm{Ph{\cdot}CH}\\ \|\\ \mathrm{HN{\cdot}OH}\\ |\\ \mathrm{Cl}\end{array}$$

anti. m. p. 105°

intermediate m. p. 63°

syn. m. p. 103°.

These authors found, however, that the "intermediate" hydrochloride is formed by recrystallising the so-called *anti*-oxime hydrochloride from chloroform; it follows that recrystallisation causes the migration of a *chlorine* atom to give a more stable hydrochloride. In this compound, tervalent nitrogen is attached to carbon, hydrogen, and hydroxyl, giving a β-α-chlorobenzylhydroxylamine; this would be a stable compound which does not appear to have been described in the literature, but it is difficult to consider that it would lose hydrogen chloride so readily. In addition, it may be mentioned that Luxmoore (*loc. cit.*, p. 182), basing his argument on the relative stabilities of the hydrochloride, hydrobromide, and hydriodide of benz*anti*aldoxime, rejects the possibility of the halogen occupying the median position as represented by Brady and Dunn.

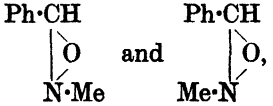
Hantzsch (" Grundriss ") invariably represents hydrochlorides as :NOH,HCl; Werner (" Lehrbuch ") does not give a single formula for an oxime hydrochloride, and his views are therefore equally difficult to gauge.

The relatively unstable character of the hydrochlorides formed by oximes has led to the conclusion that they are "oxonium" compounds, and not due to conversion of tervalent into quinquevalent nitrogen. This suggestion does not appear to have been previously considered; for example, Knox and Richards (T., 1919, **115,** 508) give a summary of "oxonium" compounds which have been prepared, but do not mention oxime hydrochlorides, and Brady and Dunn omit the possibility of "oxonium" hydrochlorides being formed, although they suggest quadrivalent oxygen to explain the action of Grignard's reagent on the *O*-methyl ethers of oximes (*loc. cit.*, p. 664). Knox and Richards (*loc. cit.*, p. 510) fail to see any reason for assigning special kinds of valency to oxygen in "oxonium" compounds any more than to other members of the same group; moreover, they mention that there is considerable evidence of the existence of "oxonium" compounds in solution (see also Rördam, *J. Amer. Chem. Soc.*, 1915, **37,** 557).

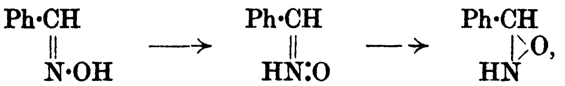
The properties of the hydrochlorides are being further investigated, and an explanation of the interconversion of oximes based on the "oxonium" character of their hydrochlorides appears possible.

Formation of Ethers by Oximes.

The main criticism of the Hantzsch-Werner hypothesis has been the undoubted existence of *N*-ethers of oximes, for which Hantzsch (" Grundriss," p. 120) found it necessary to assume the *iso*oxime formula of Beckmann, assigning to the two *N*-ethers of benzaldoxime prepared by Luxmoore (T., 1897, **69**, 177) the position formulæ

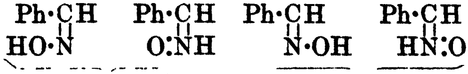


although he is obviously not clear (by his reference to p. 61) how this is feasible on the basis of the Hantzsch-Werner hypothesis. Werner (" Lehrbuch," p. 235) gives the same formulæ, and states (p. 277) that the *N*-ether is the main product from *syn*-aldoximes, whereas the *anti*-aldoximes give mainly the *O*-ether, but he does not advance any explanation. Although such formulation may appear practical on paper, it could only be produced through an intermediate compound containing quinquevalent nitrogen as follows :



that is, unless we assume the breaking of the rigid valency between the nitrogen and oxygen which has so far maintained the separate entity of the isomerides, the so-called *anti*-oxime might conceivably give a *syn*-*N*-ether, and vice versa (compare Luxmoore, *loc. cit.*, p. 188).

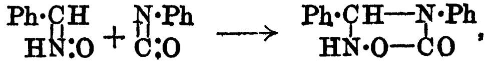
An alternative explanation of the existence of *N*-ethers is suggested by Brady and Dunn (T., 1916, **109**, 659), who assume that the oximes and their sodium salts are tautomeric substances capable of reacting in the forms :



$$\underbrace{\begin{array}{c}\text{Ph·CH}\\ \|\\ \text{HO·N}\end{array}\quad\begin{array}{c}\text{Ph·CH}\\ \|\\ \text{O:NH}\end{array}}_{\text{Benz}anti\text{aldoxime.}}\qquad\underbrace{\begin{array}{c}\text{Ph·CH}\\ \|\\ \text{N·OH}\end{array}\quad\begin{array}{c}\text{Ph·CH}\\ \|\\ \text{HN:O}\end{array}}_{\text{Benz}syn\text{aldoxime.}}$$

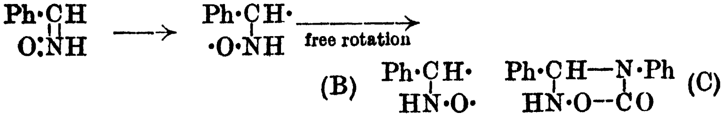
Benz*anti*aldoxime. Benz*syn*aldoxime.

It will be noted that the tautomeric forms of the stereoisomerides depend for their separate identity on the definite position of a labile hydrogen atom. Moreover, in attempting an explanation of their confirmation of the observation of Beckmann (*Ber.*, 1890, **23**, 1683) that phenylcarbimide gives with benz*anti*aldoxime the carbanilino-derivative of benz*syn*aldoxime, which was later converted into the normal derivative, these authors represent the condensation as follows:

(A) 

$$\begin{matrix}\mathrm{Ph{\cdot}CH}\\ \mathrm{HN{:}O}\end{matrix} + \begin{matrix}\mathrm{N{\cdot}Ph}\\ \mathrm{C{:}O}\end{matrix} \longrightarrow \begin{matrix}\mathrm{Ph{\cdot}CH{-}N{\cdot}Ph}\\ \mathrm{HN{\cdot}O{-}CO}\end{matrix},$$

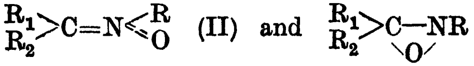
whereas the condensation with benz*anti*aldoxime is represented thus:



$$\begin{matrix}\mathrm{Ph{\cdot}CH}\\ \mathrm{O{:}NH}\end{matrix} \longrightarrow \begin{matrix}\mathrm{Ph{\cdot}CH{\cdot}}\\ \mathrm{{\cdot}O{\cdot}NH}\end{matrix} \xrightarrow[\text{free rotation}]{} \text{(B)}\ \begin{matrix}\mathrm{Ph{\cdot}CH{\cdot}}\\ \mathrm{HN{\cdot}O{\cdot}}\end{matrix} \quad \begin{matrix}\mathrm{Ph{\cdot}CH{-}N{\cdot}Ph}\\ \mathrm{HN{\cdot}O{-}CO}\end{matrix}\ \text{(C)}$$

This is scarcely an explanation, as formula (B) is identical with formula (A) already assigned by these authors to benz*syn*aldoxime, and merely assumes that phenylcarbimide first converts the so-called *anti-* into the *syn*-isomeride.

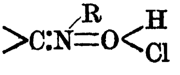
The structural theory of oxime isomerism would appear to indicate the possible existence of two *N*-ethers, thus:

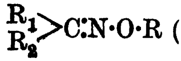


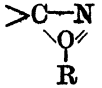
$$\begin{matrix}R_1\\R_2\end{matrix}\!>\!C{=}N\!<\!\begin{matrix}R\\O\end{matrix}\ \text{(II) and}\ \begin{matrix}R_1\\R_2\end{matrix}\!>\!\underset{\diagdown O \diagup}{C{-}NR}\ \text{(III)}.$$

Scheiber (*Annalen*, 1909, **356**, 215) states the two *N*-ethers of benzaldoxime prepared by Luxmoore (*loc. cit.*, p. 183) are identical, one *N*-ether being the hydrated form, although it is to be noted that Luxmoore (*loc. cit.*, p. 186) is obviously aware of the possibility that his *N*-ethers may contain water of crystallisation by his reference to Goldschmidt (*Ber.*, 1892, **25**, 2573).

Staudinger and Miescher (*loc. cit.*) have definitely proved that the stable *N*-ethers of ketoximes have the " nitrone " formula.

These *N*-ethers form hydrochlorides which cannot be of the " ammonium " type, and they must therefore be of the " oxonium " type:  $>C{:}\overset{\diagup R}{N}{=}O\!<\!\begin{matrix}H\\Cl\end{matrix}$ (II).

The structural theory of the isomerism of oximes admits the possible existence of only one *O*-ether derived from the so-called *anti*-oxime and having the " oxime " formula:  $\begin{matrix}R_1\\R_2\end{matrix}\!>\!C{:}N{\cdot}O{\cdot}R$ (I).

A formulation of a second *O*-ether as  $\begin{matrix}>C{-}N\\ \diagdown O \diagup\\ |\\ R\end{matrix}$ seems improbable, although similar " oxonium " compounds have been described by Kehrmann and Bohn (*Ber.*, 1914, **47**, 3052). If this formula were admitted, it would be readily converted into the more stable $>C{:}N{\cdot}O{\cdot}R$.

Forster and Dunn (T., 1909, **95**, 426) state that a "more convincing argument for the stereochemical hypothesis depends on the fact that many pairs of *O*-ethers exist, of which the *syn*-forms are readily convertible into the isomerides"; these authors do not give the references. The current view is probably based on the lists of two (supposed oxygen) ethers given, for example, in Werner's "Lehrbuch." The numerous references given by Werner ("Lehrbuch," pp. 244, 253) have been investigated, and, contrary to the assumption of Werner, give no proof whatever that the two ethers known to exist are *O*-ethers. The melting points of only two isomeric ethers of the aldoximes and of the ketoximes are tabulated, although a specific case, without the original reference, is mentioned (p. 234), namely, *m*-nitrobenzaldoxime, which is stated to give one *N*-ether and two *O*-ethers.

Semper and Lichtenstadt (*Ber.*, 1918, **51**, 928) appear to have isolated *O*-ethers of both the *anti*- and *syn*-isomerides of phenyl *p*-tolyl ketoxime, but whereas the *anti*-*O*-ether is described as of definite melting point, these authors have been unable to crystallise the *syn*-*O*-ether, of which the only identification given is its boiling point in high vacuum. This is the only case published in which four supposed stereoisomeric ethers are described.

A search through the literature has therefore failed to reveal any satisfactory proof of the existence of two definite crystalline *O*-ethers and two *N*-ethers prepared from two isomeric oximes of undoubted purity. On the contrary, Forster and Dunn (T., 1909, **95**, 425) state that diazomethane gives an *O*-methyl ether only with the so-called *anti*-aldoximes, and further remark that there is some evidence that *syn*-oximes, for example, *a*-benzilmonoxime, give *N*-ethers.

Although the *N*-ethers and the free oximes give hydrochlorides, it is to be noted that the *O*-ethers fail to give hydrochlorides; this would be anticipated if the oxime hydrochlorides are of the "oxonium" type. Brady and Dunn (T., 1916, **109**, 665) find difficulty in attempting an explanation of this fact on the basis that a hydrochloride of the "ammonium" type is formed.

Summary.

(1) The Hantzsch-Werner hypothesis of the stereoisomerism of oximes is criticised in view of the fact that it fails to explain characteristic reactions of the so-called *syn*- and *anti*-oximes, their mode of interconversion, etc., and further fails to interpret the Beckmann reaction as applied to the benzildioximes.

(2) A new structural theory of the isomerism of the oximes is

advanced which explains satisfactorily the number of isomerides known to exist, the differences in the salt-forming properties of the oxime groups present in isomeric oximes, and the formation of *O*- and *N*-ethers respectively from isomeric oximes.

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CXXXII.—*The Structural Isomerism of the Oximes. Part II. A Fourth Benzildioxime.*

By Frederick William Atack and Leonard Whinyates.

The Hantzsch-Werner hypothesis has received very material support from the isolation of the actual number of isomeric oximes which should exist if the hypothesis were correct. The existence of three isomeric methylbenzhydroximic acids, acknowledged by Werner, and of three modifications of benzaldoxime, anisaldoxime, and cuminaldoxime, whereas only two isomerides should exist in each case, has already been mentioned in the preceding communication.

It has now been found that a fourth benzildioxime (δ) may be obtained readily from α-benzildioxime or direct from α-benzilmonoxime, whereas the Hantzsch-Werner hypothesis only allows of the existence of three isomerides. According to the theory advanced by one of the present authors in the preceding communication, it might be possible to prepare six isomerides.

On dissolving α-benzildioxime (m. p. 237°) in dilute sodium hydroxide solution, and allowing to stand for the necessary time, addition of ammonium chloride precipitates the new δ-isomeride (m. p. 217°). The action of alkaline hydroxylamine solution on α-benzilmonoxime has generally been assumed to give α-benzildioxime, as this product is obtained on acidifying the solution; if the oxime is separated by addition of ammonium chloride, the δ-isomeride is precipitated.

The δ-isomeride is characterised by the formation of a buff-coloured nickel compound on addition of a slightly ammoniacal solution of a nickel salt to the sodium hydroxide solution of the dioxime; the compound is similar in colour to those given by γ-benzildioxime (Atack, T., 1913, **103**, 1317) and α-benzilmonoxime, but differs from these compounds, produced in a similar manner, by the facility with which it passes into the red nickel compound of α-benzildioxime. This conversion takes place very slowly on allowing to stand in absence of light, slowly in presence of light, and almost immediately on addition of an excess of ammonium chloride to the sodium hydroxide solution, or on heating. The conversion may be followed readily by taking advantage of the much more rapid solution in potassium cyanide solution of the buff nickel compound of the δ-dioxime as compared with the red nickel compound of the α-dioxime. On filtering off the nickel compound of the δ-dioxime and washing with cold water, it was found to be converted into the red α-dioxime compound on boiling with water.

The new isomeride is very unstable in presence of solvents, passing rapidly in alcohol solution in presence of acids or ammonia into the α-isomeride. It has not so far proved possible to recrystallise the δ-isomeride. There is no doubt, however, of its definite existence in the solid state and in solution. Thus, addition of an ammoniacal solution of a nickel salt to a freshly-prepared solution of α-benzildioxime in dilute sodium hydroxide solution gives an immediate precipitate of the characteristic red nickel compound, whereas the buff-coloured nickel compound of the δ-isomeride is produced if the solution has been allowed to stand for the necessary time before addition of the nickel solution. Moreover, a freshly prepared solution of δ-benzildioxime in neutral alcohol gives with a slightly ammoniacal nickel solution the buff nickel compound, whereas an alcoholic solution of the α-isomeride invariably gives the characteristic red nickel compound.

That the change is not simply from an unstable to a stable nickel compound of the α-benzildioxime is shown by the immediate formation of the stable red nickel compound by the freshly-prepared sodium hydroxide solution, especially if alcohol is added to retard the conversion. In addition, although the sodium hydroxide stabilises the nickel compound of δ-benzildioxime to some extent, the compound gradually passes into the red isomeride on allowing to stand, and so far it has not proved possible to isolate sufficient for analysis. Moreover, the nickel compound of the δ-dioxime dissolves readily in chloroform to a lemon-yellow solution, whereas the corresponding α-compound is only sparingly soluble.

In view of the proximity of the melting point of the δ-benzildioxime to that of the β-isomeride, it should be pointed out that it has already been shown by one of us (*loc. cit.*) that β-benzildioxime does not form a nickel salt. The benzoyl compounds obtained under identical conditions by the Schotten-Baumann reaction from the β- and δ-dioximes had m. p. 144° and 182° respectively. Acetylation of the α- and β-dioximes gave acetyl compounds of m. p. 154°

and 130° respectively (Auwers states 148° and 125°); under the same conditions the δ-dioxime failed to give an acetyl compound, but on prolonged treatment gave the acetyl compound of the α-isomeride.

The presumed conversion of β-benzildioxime into the α- and γ-isomerides (Atack, *loc. cit.*) has since been found to be due to the presence of α-benzildioxime, which cannot be removed from β-benzildioxime even by repeated recrystallisation. A sample of β-benzildioxime (m. p. 212°), twice recrystallised from alcohol after all the α-isomeride had been removed by precipitation with nickel, failed to show any conversion into the α-isomeride after allowing to stand for two days with sodium hydroxide solution. The formation of the nickel salt of the new isomeride described above would account for the presumed formation of the γ-dioxime, as detected by the addition of an ammoniacal nickel solution.

The formation of the buff nickel compound explains the yellow shade of the microcrystalline precipitate which has occasionally been obtained in the estimation of nickel by means of α-benzildioxime (Atack, *Analyst*, 1913, **38**, 317). It also explains the nature of the precipitate obtained in detecting nickel by this reagent, using a solution in sodium hydroxide, which was suggested owing to its slight solubility in alcohol (*Chemists' Year Book*, 1920 ed., p. 69); for this test it was already known to be essential to have ammonium chloride present in the solution under examination for nickel, as otherwise a buff precipitate is obtained instead of the characteristic red compound.

The constitution of the new isomeride and of the α-, β-, and γ-benzildioximes will be the subject of a later communication, and appears to be quite capable of explanation on the lines indicated by one of us in a previous communication, and its probable existence was in fact predicted by the structural theory of the isomerism of oximes.

EXPERIMENTAL.

Preparation of δ-Benzildioxime from α-Benzildioxime.

0·5 Gram of α-benzildioxime (m. p. 237°) was dissolved in 20 c.c. of cold sodium hydroxide solution (5 per cent.), allowed to stand for two hours, diluted with an equal volume of water, and ammonium chloride added. The precipitate was filtered off immediately, washed with water, and dried rapidly on a porous tile (yield 0·43 gram). The white powder obtained melted sharply at 217° to a clear brown liquid. On warming with dilute sodium hydroxide solution, no ammonia was produced. On drying at 98°, the loss in weight amounted to 1·5 per cent., which must be due to adherent moisture, and the melting point was raised slightly, to 220°.

Variation of the preparation by altering the concentration and method of admixture, and by precipitating at 0°, failed to alter the sharp melting point of 217° for the air-dried product.

Preparation of δ-Benzildioxime from α-Benzilmonoxime.

Two grams of α-benzilmonoxime (m. p. 137°) were mixed with 8 grams of sodium hydroxide in solution and sufficient cold water was added to give a clear solution. Four grams of hydroxylamine hydrochloride were gradually added, the solution was allowed to stand for twenty-four hours, diluted with an equal volume of water, and ammonium chloride added. The precipitate was filtered off rapidly, washed with water, and dried on a porous tile, when it melted at 217° (yield 2·05 grams) (Found: N in α-dioxime [m. p. 237°]=11·34. N in δ-dioxime [m. p. 217°]=11·30 per cent.).

Conversion of δ-Benzildioxime into α-Benzildioxime.

One gram of δ-benzildioxime (m. p. 217—218°) was mixed with 20 c.c. of alcohol and a few drops of ammonia solution were added; the mixture was allowed to stand for a short time with occasional shaking, and then filtered. The residue (m. p. 225°) was found to be slightly impure α-benzildioxime. On allowing the solution to evaporate, a minute residue was obtained, m. p. 216°. A similar result was obtained by the action of alcohol and a few drops of acetic acid, the melting point again being raised to 225°.

The method indicated above is being applied in the case of other oximes. It has, for example, been found that benzaldoxime oil, precipitated from the usual preparation (alkaline hydroxylamine method) by means of ammonium chloride, gives the colour tests with ferric chloride and copper acetate stated by Beck and Hase (*Annalen*, 1907, **355**, 31) to be given only by the β-isomeride, whereas the α-isomeride is the normal product isolated in this preparation.

Summary.

(1) A fourth isomeric benzildioxime (δ), m. p. 217°, has been prepared, which is sharply differentiated by the colour and behaviour of its nickel compound and by other reactions from the three known benzildioximes.

(2) The Hantzsch-Werner hypothesis only admits of the existence of three isomeric benzildioximes, whereas the structural theory

admits of six possible isomerides; the preparation of the two remaining isomerides is under investigation.

The authors desire to express their thanks to Professor Knecht for the facilities afforded for carrying out the research, the publication of which has been delayed by the interruption of research activities arising out of the war.

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CXXXIII.—*The Action of the Grignard Reagent on certain Organo-sulphur Compounds.*

By HARRY HEPWORTH and HENRY WILLIAM CLAPHAM.

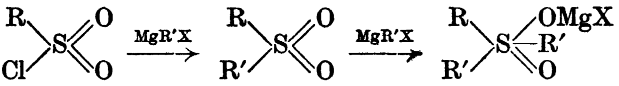
COMPARATIVELY few investigations have been carried out on the action of the Grignard reagent on sulphur compounds. Wuyts and Cosyns (*Bull. Soc. chim.*, 1903, [iii], **29**, 89) studied the action of sulphur, selenium, and tellurium on Grignard compounds, whilst Taboury (*ibid.*, 1903, [iii], **29**, 761; 1904, [iii], **31**, 1183; 1905, [iii], **33**, 836; *Compt. rend.*, 1904, **138**, 982) obtained mercaptans and sulphides in a similar manner, and further, obtained certain thiobenzoates by heating the undecomposed reaction product with acid chlorides. Somewhat later, Wuyts (*Bull. Soc. chim.*, 1909, [iv], **5**, 405) showed that disulphides were also produced in these reactions.

The action of sulphur dioxide on Grignard compounds has been investigated by Rosenheim and Singer (*Ber.*, 1904, **37**, 2152) and by Oddo (*Gazzetta*, 1911, **41**, ii, 11), whilst Strecker (*Ber.*, 1900, **43**, 1131) has studied the action of sulphur chloride, thionyl chloride, and the esters of sulphurous acid. Oddo (*Atti R. Accad. Lincei*, 1905, [v], **14**, i, 169) obtained phenylsulphinic acid, chlorobenzene, and diphenyl by the action of magnesium phenyl bromide on sulphuryl chloride.

Houben and Kesselkaul (*Ber.*, 1902, **35**, 3696) studied the action of carbon disulphide on Grignard compounds, whilst Weigert (*Ber.*, 1903, **36**, 1007) investigated the action of carbonyl sulphide.

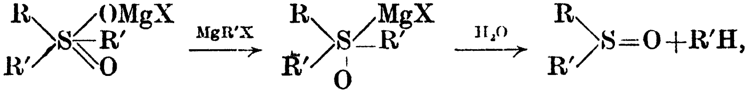
Sachs (*Ber.*, 1903, **36**, 585) studied the action of *iso*thiocyanates, whilst Adams and his collaborators (*J. Amer. Chem. Soc.*, 1920, 42, 2369) have studied the action of the Grignard reagents on thiocyanates.

In the preliminary experiments described in this paper, the action of magnesium alkyl and aryl haloids on benzenesulphonyl chloride and ethyl chlorosulphonate was investigated. The principal products obtained in all these reactions were sulphoxides, whilst sulphides, and in some cases sulphones, were formed to a smaller extent. The sulphoxides were usually obtained in good yield and these methods of preparation of the sulphoxides may be recommended on account of the ease and simplicity of preparation. In view of the formation of sulphones observed in some experiments, the course of the reaction, in the case of benzenesulphonyl chloride, may be represented as follows :



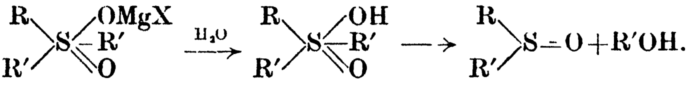
(I.) (II.)

Compound II may react further with MgR'X :



(III.) (IV.)

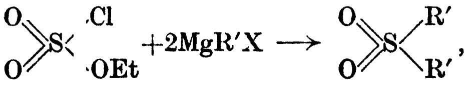
or, less likely, since the formation of alcohols and phenol was not observed :



(V.)

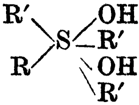
The formation of sulphides is to be explained by the further action of magnesium alkyl (aryl) haloid on II and III.

In the case of ethyl chlorosulphonate, the preliminary reaction is probably :



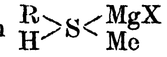
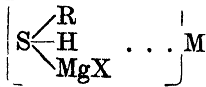
(VI.)

VI then reacts with a further quantity of MgR'X on the lines already indicated in the case of benzenesulphonyl chloride.

One of us (this vol., p. 253) has already shown that a similar reducing action, by means of Grignard reagents, takes place when the latter react with nitric esters. If no reducing action took place, and the formation of sulphides is explained by the loss of alcohols or phenol from the compound  $\mathrm{{R' \atop R}{>}S{<}{{OH \atop R'} \atop {OH \atop R'}}}$, then disulphides would be expected to be formed by the condensation of two molecules of this compound. This type of reaction has already been suggested by one of us to account for the formation of azo-compounds by the action of Grignard reagents on aromatic nitro-compounds (T., 1920, **117**, 1008).

In the course of his investigation on the estimation of hydroxylic hydrogen in organic compounds, Zerewitinoff (*Ber.*, 1908, **41**, 2233) observed the formation of paraffin hydrocarbons on treating the mercaptans with Grignard reagents, and postulated the reaction as:

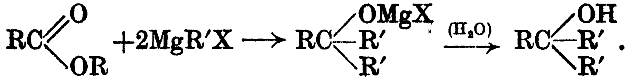
$$\mathrm{R{\cdot}SH + MgR'X = R'H + MgSRX.}$$

Zerewitinoff observed the formation of methane from propyl, *iso*butyl, *iso*amyl, phenyl, and benzyl mercaptans, whilst the authors have observed a similar reaction with ethyl and butyl mercaptans. If in these reactions addition precedes substitution, then a compound, R·SH,MgR′X, in which sulphur is quadrivalent, must be formed. If this is written  $\mathrm{{R \atop H}{>}S{<}{MgX \atop Me}}$ (where R′ is methyl), in which all the valencies are similar, there is no *a priori* reason to expect methane to be invariably evolved, independent of the nature of the radicle R. Since methane is always formed, it is reasonable to suppose that the methyl group is more feebly attached to the sulphur atom than is the radicle R. Now Abegg (*Ber.*, 1905, **38**, 4112) has suggested that the alkyl groups in magnesium alkyl haloids are negative, since these, on decomposition with water, form hydrocarbons. If this view is accepted, the negative methyl group in the above compound will be more loosely attached to the sulphur atom than the positive radicle R; this difference may be shown by the formula  $\left[\mathrm{S{<}{R \atop {H \atop MgX}} \ldots Me}\right]$, derived in accordance with Werner's views of valency. This view may be extended to explain the action of water and alcohols on magnesium alkyl and aryl haloids. The view that in oxonium "Grignard" compounds the four valencies of the oxygen atom are not all equal is by no means new. Grignard considers (*Bull. Soc. chim.*, 1907, [iv], **1**, 256) that the two additional valencies in these compounds have not the same value as the original two, whilst the abnormal reaction between magnesium β-methylanilinoethyl bromide and ketones has been explained by Braun (*Ber.*, 1919, **52**, [*B*], 1725) on similar lines.

In the experiments described in this paper, it is confirmed that the compound Mg(SEt)X is formed by the action of magnesium alkyl haloids on ethyl mercaptan, and if the product is treated with ethyl chloroformate, benzoyl chloride, or acetyl chloride, ethyl thiocarbonate (EtS·CO·OEt), ethyl thiobenzoate (PhCO·SEt), and ethyl thioacetate (CH_3·CO·SEt) are respectively formed in accordance with the general equation

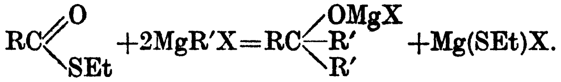
$$\mathrm{Mg(SEt)X + ClCOR(ClCO_2R) \longrightarrow EtS{\cdot}COR(EtS{\cdot}CO_2R)}.$$

It is well known that simple esters usually react with magnesium alkyl or aryl haloids with the production of tertiary alcohols, an alkyl or aryl group derived from the Grignard compound being substituted for the OR-group of the ester in accordance with the general equation :



$$\mathrm{RC}\begin{array}{l}\diagup\!\!\diagup \mathrm{O}\\ \diagdown \mathrm{OR}\end{array} + 2\mathrm{MgR'X} \longrightarrow \mathrm{RC}\begin{array}{l}\diagup \mathrm{OMgX}\\ - \mathrm{R'}\\ \diagdown \mathrm{R'}\end{array} \xrightarrow{(\mathrm{H_2O})} \mathrm{RC}\begin{array}{l}\diagup \mathrm{OH}\\ - \mathrm{R'}\\ \diagdown \mathrm{R'}\end{array}.$$

From a study of the action of the magnesium alkyl and aryl haloids on ethyl thiobenzoate, ethyl thioacetate, and ethyl thiocarbonate, it has now been shown that the SEt-group of these thio-esters is removed and that tertiary alcohols, containing no sulphur, are produced according to the equation :



$$\mathrm{RC}\begin{array}{l}\diagup\!\!\diagup \mathrm{O}\\ \diagdown \mathrm{SEt}\end{array} + 2\mathrm{MgR'X} = \mathrm{RC}\begin{array}{l}\diagup \mathrm{OMgX}\\ - \mathrm{R'}\\ \diagdown \mathrm{R'}\end{array} + \mathrm{Mg(SEt)X}.$$

On decomposing the reaction products with water, Mg(SEt)X yields the original mercaptan from which the thio-ester was derived, and this may be recovered. Triphenylcarbinol has been prepared by the action of magnesium phenyl bromide on ethyl thiobenzoate, and on ethyl thiocarbonate, whilst phenyldiethylcarbinol has been obtained by the action of magnesium ethyl bromide on ethyl thiobenzoate and diphenylmethylcarbinol by the action of magnesium phenyl bromide on ethyl thioacetate.

The action of magnesium methyl iodide and magnesium ethyl bromide on di*iso*amylsulphoxide and diphenylsulphoxide was next investigated, the reaction being carried out in dry toluene, but very little reaction took place, a little sulphide being formed, but no sulphonium bases.

Hinsberg (*J. pr. Chem.*, 1912, [ii], **85**, 337) has shown that in trimethylene trisulphoxide the SO-groups confer acidic properties on the hydrogen of the methylene groups. In a similar way, trimethylenetrisulphone is a yet stronger acid, but the hydrogen of the methylene groups does not react with diazo-salts or aldehydes.

Desmotropic compounds frequently react in the enolic form with magnesium alkyl haloids and evolve the corresponding paraffin hydrocarbon (Grignard, *Compt. rend.*, 1902, **134**, 849; McKenzie, T., 1906, **89**, 380; Hepworth, T., 1919, **115**, 1208). Trimethylene trisulphoxide and trimethylenetrisulphone were found to be unaffected by magnesium alkyl haloids, but both these compounds are almost insoluble in anisole, amyl ether, and other organic solvents. The ethyl ester of phenylsulphoneacetic acid (Michael, *J. pr. Chem.*, 1899, [ii], **60**, 96) reacts readily with magnesium methyl iodide with the production of methane, thus confirming the views of Michael (*loc. cit.*) on the tautomerism of this ester.

Finally, the action of organo-magnesium compounds on the sulphones was investigated. It was found that di*iso*amylsulphone and diphenylsulphone are remarkably stable towards magnesium alkyl and aryl haloids, and that there is no analogy between the activity of the SO_2-group in the sulphones and the CO-group in the corresponding ketones (compare Knoevenagel, *Ber.*, 1888, **21**, 1347; V. Meyer, *ibid.*, 1887, **20**, 2947). Whilst magnesium alkyl haloids have no action on phenylbenzylsulphone, Klages (*Ber.*, 1904, **37**, 1447) has shown that they react very readily with the corresponding CO-compound, deoxybenzoin.

Sache and his collaborators (*Ber.*, 1904, **37**, 385, 3252) have shown that, although saccharin and its *N*-derivatives react with Grignard compounds, the SO_2-group in these compounds is unattacked.

EXPERIMENTAL.

Action of Magnesium Phenyl Bromide, Magnesium Ethyl Bromide and Magnesium Benzyl Chloride on Benzenesulphonyl Chloride.

A mixture of 20 grams of benzenesulphonyl chloride and 50 grams of dry ether was added drop by drop to an ice-cold solution of magnesium phenyl bromide prepared from 8·3 grams (3 mols.) of magnesium, 54 grams (3 mols.) of bromobenzene, and 150 c.c. of dry ether. At first the addition of each drop of the acid chloride mixture produced a vigorous reaction and gave rise to a white precipitate. After about one-third had been added, the reaction became less vigorous, and the flask was removed from the ice-cold water. When all the mixture had been added, it was observed that the ether layer was quite clear. After remaining at the ordinary temperature for sixteen hours, the reaction mixture was warmed on a water-bath for one hour.

The upper, ethereal layer was decanted, decomposed with water, and the precipitated magnesium hydroxide dissolved in dilute sulphuric acid. On distillation, a little bromobenzene and diphenyl were obtained.

The lower, solid layer was covered with 100 c.c. of ether and cautiously decomposed with ice-cold water, followed by the addition of dilute acetic acid. After neutralisation of the ethereal layer with sodium carbonate, the ether was evaporated and the residue distilled in steam for one hour. A little benzene and diphenyl came over. The residue in the flask was then distilled in a vacuum:

1st fraction	up to	200°/20 mm.	2 grams
2nd	,,	210—212°/20 mm.	16 grams.

Fraction 1 consisted principally of diphenyl, whilst fraction 2 melted at 68—70°. After two crystallisations from benzene, a white, crystalline product, m. p. 69—70°, was obtained (M in benzene=198, 202. $(C_6H_5)_2SO$ requires M=202). A little diphenylsulphone (m. p. 128°; b. p. 232°) was obtained on working up the residue left in the flask after distillation.

In a similar experiment with 8 grams (3 mols.) of magnesium, 37 grams (3 mols.) of ethyl bromide, and 20 grams of benzenesulphonyl chloride, the products were 3 grams of phenyl ethyl sulphide, b. p. 204° (Beckmann, *J. pr. Chem.*, 1878, [ii], **17**, 439) (M in benzene=143, 144; calc., 138), 3 grams of phenyl ethyl sulphoxide (b. p. 146°/13 mm.) (Found: S=20·32, 20·47. M in benzene=152, 153. Calc. for $C_6H_5{\cdot}SO{\cdot}C_2H_5$, S=20·78 per cent. M=154), and a small quantity of phenylethylsulphone, m. p. 42° (Otto, *Ber.*, 1880, **13**, 1275).

In an experiment in which 20 grams of benzenesulphonyl chloride, 8 grams (3 mols.) of magnesium, and 43 grams (3 mols.) of benzyl chloride were employed, 10 grams of phenyl benzyl sulphoxide, m. p. 125°, were obtained after two crystallisations from alcohol (M in benzene=219, 217; calc., 216) (Pummerer, *Ber.*, 1910, **43**, 1406).

On further concentrating the mother-liquors obtained from the crystallisation of the sulphoxide, a small quantity of phenylbenzylsulphone was obtained in greyish-white, hair-like needles, which, after one crystallisation from alcohol, melted at 148° (corr.) (Knoevenagel, *Ber.*, 1888, **21**, 1349). A small quantity of phenyl benzyl sulphide, m. p. 44°, was also obtained (Pummerer, *loc. cit.*).

Action of Magnesium Phenyl Bromide and Magnesium Ethyl Bromide on Ethyl Chlorosulphonate.

A mixture of 20 grams of ethyl chlorosulphonate and 50 c.c. of dry ether was added drop by drop to an ice-cold solution of magnesium phenyl bromide prepared from 10·1 grams (3 mols.) of magnesium, 65·2 grams (3 mols.) of bromobenzene, and 100 c.c. of dry ether. A vigorous reaction ensued and the product, after remaining overnight, was decomposed with water, followed by acetic acid in the usual manner. After extraction with ether and removal of this solvent, 30 grams of a reddish-brown oil were obtained, which was distilled in a vacuum. Three fractions were collected:

Fraction 1,	up to 110°/15 mm.	7 grams
,, 2,	110—180°	5 grams
,, 3,	210—215°	14 grams
Residue		about 3 grams

Fraction 1 consisted principally of bromobenzene, fraction 2 consisted of diphenyl, whilst fraction 3, after crystallisation from benzene, melted at 70° and the melting point remained unaltered after admixture of pure diphenyl sulphoxide.

In a similar experiment with 20 grams of chlorosulphonic ester, 10·1 grams (3 mols.) of magnesium, and 45·2 grams (3 mols.) of ethyl bromide, 2 grams of diethyl sulphoxide, b. p. 88—90°/15 mm. (Pummerer, *loc. cit.*), were obtained as an uncrystallisable syrup, which, treated with fuming nitric acid, gave diethylsulphone, m. p. 70°, b. p. 248—250°, whilst 5 grams of diethyl sulphide were also obtained. A considerable quantity of the latter distilled over with the ether.

Action of Magnesium Methyl Iodide on Ethyl Mercaptan and the Preparation of Thio-esters from Magnesium Ethylthiol Bromide, Mg(SEt)Br.

Ethyl mercaptan was prepared from sodium ethylsulphate and a concentrated aqueous solution of potassium hydrosulphide, according to the method of Klason (*Ber.*, 1887, **20**, 3411). A considerable quantity of diethyl sulphide was also obtained during this preparation.

A solution of 6·2 grams of ethyl mercaptan in 50 c.c. of dry ether was added drop by drop to a clear, ice-cold solution of magnesium methyl iodide, prepared from 2·5 grams of magnesium, 14·5 grams of methyl iodide, and 50 c.c. of dry ether. A vigorous reaction ensued, the ether boiled, and a considerable quantity of methane was evolved. The white, voluminous precipitate was washed three times with dry ether and a portion of the precipitate dried in a vacuum over phosphoric oxide overnight (Found: Mg=11·50, 11·53; I=59·42, 59·53. C_2H_5ISMg requires Mg=11·41; I=59·62 per cent.).

In a similar manner, methane was evolved on treating *n*-butyl mercaptan with magnesium methyl iodide.

To an ice-cold ethereal mixture of magnesium ethylthiol bromide, prepared in a similar way from 11 grams of ethyl mercaptan, 22 grams of ethyl bromide, and 5 grams of magnesium, 28 grams of benzoyl chloride in 60 c.c. of dry ether were slowly added, whereby a vigorous reaction was initiated. After the addition was complete, the mixture was heated on a water-bath for three hours, cooled, and decomposed with ice-cold water. The product was extracted with ether, and after drying the ethereal extract and removing the ether, the residual oil was fractionated. After two fractionations 20 grams of ethyl thiobenzoate, b. p. 241—243° (corr.), were obtained.

In a similar manner, 16 grams of ethyl thiocarbonate, b. p. 153—155° (corr.), were obtained from 10·4 grams of ethyl mercaptan, 20 grams of ethyl bromide, 5 grams of magnesium, and 19 grams of ethyl chloroformate, whilst 12 grams of ethyl thioacetate, b. p. 116—117°, were obtained from similar quantities of magnesium, ethyl bromide, ethyl mercaptan, and 12 grams of acetyl chloride.

Action of Magnesium Ethyl Bromide and of Magnesium Phenyl Bromide on Ethyl Thiobenzoate, and of Magnesium Phenyl Bromide on Ethyl Thioacetate and on Ethyl Thiocarbonate.

A solution of magnesium ethyl bromide prepared from 3·1 grams (2·5 mols.) of magnesium, 13·6 grams of ethyl bromide, and 20 c.c. of dry ether was slowly added to a solution of 7 grams (1 mol.) of ethyl thiobenzoate in 20 c.c. of dry ether, the ensuing vigorous reaction being moderated by immersing the flask in ice-cold water. A voluminous precipitate was formed. The mixture was now heated on a water-bath for two and a half hours, and, after remaining overnight, was decomposed with ice-cold water, followed by sufficient dilute sulphuric acid to dissolve the whole of the precipitated magnesium hydroxide. The ethereal layer, which had a powerful odour of mercaptan, was separated, the contents of the flask extracted three times with ether, and the ethereal solution dried and distilled. One and a half grams of ethyl mercaptan were recovered from the ether by repeated extraction with 25 per cent. sodium hydroxide and subsequent acidification with concentrated hydrochloric acid. On distillation of the residue after evaporation of the ether, the main fraction boiled at 220—226° (corr.), whilst on redistillation 6 grams of phenyldiethylcarbinol, b. p. 223—224° and 124—125°/10 mm. (Kling, *Compt. rend.*, 1903, **137**, 758), were obtained.

From 7 grams of ethyl thiobenzoate, 3·1 grams of magnesium and 20 grams of bromobenzene, 8 grams of triphenylcarbinol, m. p. 161°, were obtained. The carbinol was separated from diphenyl by distillation in steam, when the latter passed over. The carbinol crystallised in hexagonal rhombohedra from benzene, and gave a yellow colour with cold concentrated sulphuric acid.

From 3·5 grams of ethyl thioacetate, and magnesium phenyl bromide prepared from 2·1 grams (2·5 mols.) of magnesium and 13 grams of bromobenzene, 5 grams of methyldiphenylcarbinol, m. p. 80—81° (Klages, *Ber.*, 1902, **35**, 2646), were obtained in prisms (from ether). After two distillations at the ordinary pressure, 3·5 grams of *as*-diphenylethylene, b. p. 269—271°, were obtained (Masson, *Compt. rend.*, 1902, **135**, 533).

In a similar manner, 7 grams of ethyl thiocarbonate, 5 grams of magnesium (4 mols.), and 31 grams of bromobenzene gave 13 grams of triphenylcarbinol, m. p. 161·5°.

*Action of Magnesium Ethyl Bromide and of Magnesium Phenyl Bromide on Di*iso*amyl Sulphoxide, Diphenyl Sulphoxide, Phenyl Benzyl Sulphoxide and Trimethylene Trisulphoxide.*

Di*iso*amyl sulphoxide was prepared by the oxidation of di*iso*amyl sulphide with 30 per cent. hydrogen peroxide according to the method of Smiles (T., 1908, **93**, 1833).

Trimethylene trisulphoxide was obtained by the oxidation of trimethylene trisulphide in glacial acetic acid with 30 per cent. hydrogen peroxide according to the method of Hinsberg (*J. pr. Chem.*, 1912, [ii], **85**, 337).

Five grams of diphenyl sulphoxide were added to an ethereal solution of magnesium methyl iodide, prepared from 2·3 grams (4 mols.) of magnesium, 14 grams of methyl iodide, and 35 c.c. of dry ether. No evident reaction took place, even on warming for four hours on a water-bath. The bulk of the ether was removed, 50 c.c. of dry toluene were added, and the mixture was heated for twelve hours. After decomposition in the usual way, extraction with ether and distillation of the oil obtained after removal of the ether, 2·5 grams of diphenyl sulphide (b. p. 294—296°) and 2·2 grams of unchanged diphenyl sulphoxide (m. p. 70°; b. p. 210°/15 mm.) were obtained. No sulphonium base was formed during the reaction.

The reaction between magnesium phenyl bromide and diphenyl sulphoxide or di*iso*amyl sulphoxide in dry toluene is very much slower than with magnesium ethyl bromide. From 5 grams of diphenyl sulphoxide and magnesium phenyl bromide, only 1·5 grams of diphenyl sulphide were obtained after fifteen hours' heating, whilst no sulphonium base was formed. In a similar experiment with 5 grams of di*iso*amyl sulphoxide, 3 grams of magnesium and 19 grams of methyl iodide, 3 grams of di*iso*amyl sulphide (b. p. 213—215°) were obtained.

Five grams of phenyl benzyl sulphoxide, 2·3 grams of magnesium (3·2 mols.), and 14 grams of methyl iodide, when heated for fifteen hours in toluene containing a few c.c. of ether, gave 2 grams of phenyl benzyl sulphide, m. p. 44° (Pummerer, *loc. cit.*), and 2·5 grams of unchanged phenyl benzyl sulphoxide.

In order to ascertain whether phenyl benzyl sulphoxide or trimethylene trisulphoxide had any tendency to react in the enolic form with Grignard compounds, the following experiments were carried out.

A round-bottomed flask of 150 c.c. capacity, carrying a side-tube attached to a Lunge nitrometer containing dry mercury, was thoroughly dried and 20 c.c. of dry anisole, previously distilled over sodium and afterwards over phosphoric oxide, together with 10 c.c. of a solution in anisole of magnesium methyl iodide, free from methyl iodide, were added. A small test-tube containing 0·15 gram of either of the above sulphoxides was carefully placed in the flask, which was then immersed in a thermostat at 70°. When the pressure had become constant, usually after two to three hours, the flask was shaken so as to bring the sulphoxide into intimate contact with the Grignard compound. No appreciable increase in volume took place, even when heating was continued for an hour after mixing.

Action of Magnesium Methyl Iodide on Diphenylsulphone, Phenylbenzylsulphone, Trimethylenetrisulphone, and Ethyl Phenylsulphoneacetate.

Diphenylsulphone was prepared by the action of benzenesulphonyl chloride on benzene in the presence of aluminium chloride, according to the method of Beckurts and Otto (*Ber.*, 1878, **11**, 2066). Trimethylenetrisulphone was prepared by the action of potassium permanganate on trithioformaldehyde (Camps, *Ber.*, 1892, **25**, 234), whilst ethyl phenylsulphoneacetate was obtained by the action of ethyl chloroacetate on sodium benzenesulphinate (Michael, *loc. cit.*).

Five and a half grams of diphenylsulphone were added to a solution of magnesium methyl iodide prepared from 2·1 grams (4 mols.) of magnesium, 13 grams of methyl iodide, and 30 c.c. of dry ether. No reaction took place on heating on the water-bath for four hours. The bulk of the ether was removed, 50 c.c. of dry toluene were added, and the flask was heated on a sand-bath for eighteen hours. After decomposing the product in the usual way, 4 grams of unchanged diphenylsulphone were recovered. No diphenyl sulphide or sulphonium base was detected. Similar results were obtained with phenylbenzylsulphone and trimethylenetrisulphone, even when anisole was substituted for toluene as solvent medium.

Ethyl phenylsulphoneacetate (0·1 gram) was allowed to react with excess of magnesium methyl iodide in dry anisole in the apparatus already used for studying the action of the same Grignard compound on phenyl benzyl sulphoxide. There was a vigorous reaction, much gas was evolved, and after half an hour 8·9 c.c. (at N.T.P.) of methane were collected (calc. on the basis of the reaction, $C_6H_5{\cdot}SO_2{\cdot}CH_2{\cdot}CO_2Et+MgMeI$, $CH_4=9{\cdot}82$ c.c.).

Further experiments are being carried out in these laboratories on the action of Grignard reagents on the ethyl esters of phenyl- and ethyl-thiolacetic acids in the hope of obtaining corresponding tertiary alcohols containing sulphur.

The authors are indebted to the Research Committee of Messrs. Nobel's Explosives Company, Limited, and particularly to Mr. Rintoul, for the facilities accorded them in carrying out this investigation.

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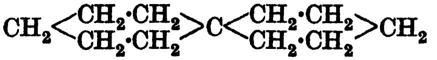
Ardeer Factory,
Stevenston, N.B.

[*Received, May* 13*th*, 1921.]

CXXXIV.—*The Formation and Stability of* spiro-*Compounds. Part V. Derivatives of* cyclo*Hexane*spirocyclo*hexane and of* cyclo*Pentane*spirocyclo*hexane.*

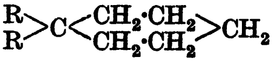
By Woodford Stanley Gowan Plucknette Norris and
Jocelyn Field Thorpe.

In the study of *spiro*-compounds which is now being carried out in these laboratories, and as the outcome of which it is hoped to gain some insight into the nature of valency as it occurs in carbon compounds, the substances hitherto dealt with have been those which contained groups attached to the carbon atoms of the spirane hydrocarbons, and conclusions have been drawn by comparing the stability of such systems with corresponding compounds of other series. It is evident, however, that valuable evidence will be obtained by comparing the stability of the spirane hydrocarbons themselves, such as, for example, *cyclo*hexane*spirocyclo*hexane (I) and *cyclo*pentane*spirocyclo*hexane (II).



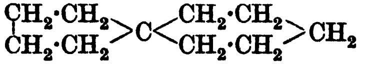
$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH_2$

(I.)



$\begin{matrix}R\\ R\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH_2$

(III.)

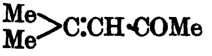


$\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH_2$

(II.)

Moreover, the comparison of these hydrocarbons and their derivatives with similar hydrocarbons of type (III) will afford valuable evidence concerning the ease of formation and stability of similarly constituted systems.

It is apparent that the best way to prepare hydrocarbons and derivatives of hydrocarbons of types (I) and (II) would be to utilise the reaction by which Vorländer (*Annalen*, 1897, **294**, 253) had obtained dimethyldihydroresorcinolcarboxylic ester (IV) from ethyl (sodio)malonate (V) and mesityl oxide (VI), because not only

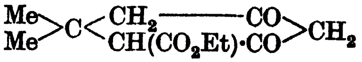


$\begin{matrix}Me\\ Me\end{matrix}>C{:}CH\cdot COMe$

(VI.)

$CH_2(CO_2Et)_2$

(V.)

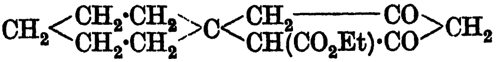


$\begin{matrix}Me\\ Me\end{matrix}>C<\begin{matrix}CH_2\text{———}CO\\ CH(CO_2Et)\cdot CO\end{matrix}>CH_2$

(IV.)

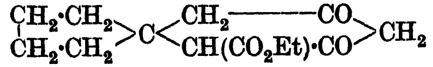
does the reaction proceed smoothly and under easily controlled conditions, but also because a method for the preparation of the hydrocarbons from this and analogous compounds has been worked out by Crossley and his collaborators.

At first sight it did not seem as if it would be an easy matter to obtain the two compounds (VII) and (VIII) which are analogous



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2}\text{———————}\mathrm{CO}\\\mathrm{CH(CO_2Et)\cdot CO}\end{matrix}>\mathrm{CH_2}$$

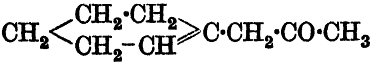
(VII.)



$$\begin{matrix}\mathrm{CH_2\cdot CH_2}\\|\\\mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2}\text{———————}\mathrm{CO}\\\mathrm{CH(CO_2Et)\cdot CO}\end{matrix}>\mathrm{CH_2}$$

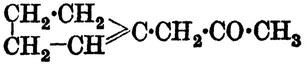
(VIII.)

to dimethyldihydroresorcinolcarboxylic ester and which would form the basis of this investigation, because the only ketones allied to mesityl oxide in the cyclic series which have hitherto been prepared are *cyclo*hexenylacetone (IX) (Wallach, *Annalen*, 1912, **394**, 362), and *cyclo*pentenylacetone (X) (Kon, this vol., p. 823).



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2-CH}\end{matrix}\geqslant\mathrm{C\cdot CH_2\cdot CO\cdot CH_3}$$

(IX.)

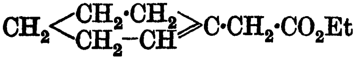


$$\begin{matrix}\mathrm{CH_2\cdot CH_2}\\|\\\mathrm{CH_2-CH}\end{matrix}\geqslant\mathrm{C\cdot CH_2\cdot CO\cdot CH_3}$$

(X.)

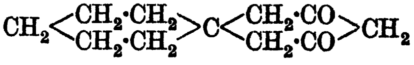
Wallach's ketone (IX) was prepared by the condensation of *cyclo*hexanone and acetone. It was also prepared by Kon (*loc. cit.*) from the calcium salt of *cyclo*hexanediacetic acid on distillation, and there could be no question that the two substances were identical, since they had the same refractive index and gave identical semi-carbazones. It was evidently the absence of exaltation in the refractive power which led Wallach to place the double bond of his compound within the ring, and a similar formula was therefore assigned by Kon to the ketone (X) which he had obtained by distilling the calcium salt of *cyclo*pentanediacetic acid, a ketone which also failed to give a refractive power having the required exaltation for a double bond outside the ring.

It did not seem likely, therefore, assuming the physical evidence of structure to be conclusive, that the desired condensation product could be obtained from these ketones, especially as Harding, Haworth, and Perkin (T., 1908, **93**, 1949) have shown that in the case of the similarly constituted *cyclo*hexenylacetic ester (XI)



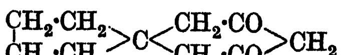
$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2-CH}\end{matrix}\geqslant\mathrm{C\cdot CH_2\cdot CO_2Et}$$

(XI.)



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2\cdot CO}\\\mathrm{CH_2\cdot CO}\end{matrix}>\mathrm{CH_2}$$

(XII.)



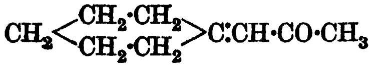
$$\begin{matrix}\mathrm{CH_2\cdot CH_2}\\|\\\mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2\cdot CO}\\\mathrm{CH_2\cdot CO}\end{matrix}>\mathrm{CH_2}$$

(XIII.)

no condensation product is formed with ethyl sodiocyanoacetate and that, in fact, the rule regarding the inability of βγ-unsaturated ketones and esters to undergo the "Michael" condensation is strictly adhered to.

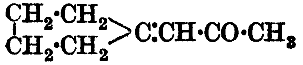
Nevertheless, in view of its importance for our work, we were led to try the condensation of the ketones (IX) and (X) with ethyl sodiomalonate in order to find whether under special experimental conditions it would be possible to induce interaction to occur, and we were, therefore, greatly surprised to find that under the usual Vorländer conditions a 70—80 per cent. yield of the normal condensation products (VII) and (VIII) were obtained. These compounds, in the hydrated form in which they are always isolated, are crystalline solids which pass on hydrolysis into the dihydroresorcinol derivatives (XII) and (XIII).

We do not consider, on the chemical evidence, that there can be any reason to doubt that the formulæ assigned by Wallach to the ketone (IX) and by Kon to the ketone (X) are incorrect, and that the real structures of these compounds should be represented by the formulæ (XIV) and (XV).



$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C:CH\cdot CO\cdot CH_3$$

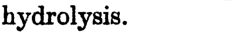
(XIV.)



$$\begin{array}{l}CH_2\cdot CH_2\\ \vert\\ CH_2\cdot CH_2\end{array}>C:CH\cdot CO\cdot CH_3$$

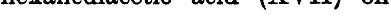
(XV.)

Experiments on the oxidation of these ketones are now in progress, and it is hoped that these will supply confirmatory evidence, but, on the other hand, compounds of this type are not easy to oxidise and often fail to give readily recognisable products. It was, therefore, with the object of strengthening the chemical evidence in favour of formulæ (XIV) and (XV) that we have extended the negative evidence supplied by Harding, Haworth, and Perkin by condensing *cyclo*hexylideneacetic ester (XVI) with ethyl sodiocyanoacetate, and we have obtained in this way a cyano-ester, from which we have prepared *cyclo*hexanediacetic acid (XVII) on hydrolysis.



$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C:CH\cdot CO_2Et$$

(XVI.)

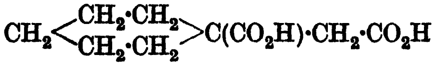


$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

(XVII.)

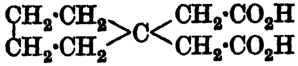
There is, then, definite proof that the βγ-ester (XI) does not undergo the "Michael" condensation and that the αβ-ester (XVI) does so, and it would, we think, be unreasonable to suppose that the corresponding ketones do not behave in the same way.

The constitutions of the *spiro*-derivatives (XII) and (XIII) were confirmed by oxidation. *cyclo*Hexane*spirocyclo*hexane-3 : 5-dione (XII) gave *cyclo*hexane-1 : 1-diacetic acid (XVII) on oxidation with hypobromite, and *cyclo*hexane-1-acetic-1-carboxylic acid (XVIII) on oxidation with alkaline permanganate.



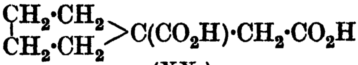
$$CH_2<\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}>C(CO_2H)\cdot CH_2\cdot CO_2H$$

(XVIII.)



$$\substack{CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2}>C<\substack{CH_2\cdot CO_2H\\ CH_2\cdot CO_2H}$$

(XIX.)

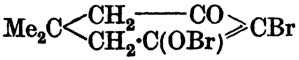


$$\substack{CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2}>C(CO_2H)\cdot CH_2\cdot CO_2H$$

(XX.)

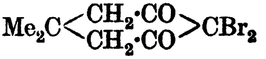
In the same manner *cyclo*pentane*spirocyclo*hexane-3 : 5-dione (XIII) gave, with hypobromite, *cyclo*pentane-1 : 1-diacetic acid (XIX), and with alkaline permanganate, *cyclo*pentane-1-acetic-1-carboxylic acid (XX).

It will be noticed that in his work on dimethyldihydroresorcinol, Vorländer (*loc. cit.*) prepared the dibromo-derivative by the action of excess of bromine on the diketone. He observed that one of the bromine atoms in the dibromo-compound was readily removed by alkali, but that the other could not be replaced even by prolonged boiling with strong aqueous alkali hydroxide. He therefore considered that formula (XXI) best represented the reactions of the substance.



$$Me_2C<\substack{CH_2\text{——}CO\\ CH_2\cdot C(OBr)}>CBr$$

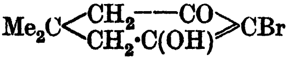
(XXI.)



$$Me_2C<\substack{CH_2\cdot CO\\ CH_2\cdot CO}>CBr_2$$

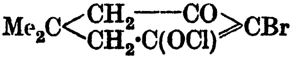
(XXII.)

The suggested formula is a peculiar one, because there are few organic compounds in which the presence of the grouping OBr can be definitely established. Moreover, there is no essential difference between the behaviour of the dibromo-compound and, for example, the dibromo-derivatives of substituted malonamides described by Backes, West, and Whiteley (this vol., p. 359), although in these and similar cases the second bromine atom is removed with greater ease. Owing to the high tendency to crystallise which the derivatives of dihydroresorcinol possess, it is, as it happens, a simple matter to put the Vorländer formula to experimental proof and we have done this by first preparing the monobromo-derivative (XXIII) and then chlorinating it to the bromochloro-derivative, which, if Vorländer were right, would have the formula (XXIV).



$$Me_2C<\substack{CH_2\text{——}CO\\ CH_2\cdot C(OH)}>CBr$$

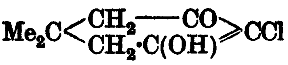
(XXIII).



$$Me_2C<\substack{CH_2\text{——}CO\\ CH_2\cdot C(OCl)}>CBr$$

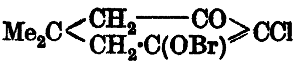
(XXIV.)

We have then reversed the process and have prepared the monochloro-derivative (XXV), which we have subsequently brominated to the chlorobromo-derivative (XXVI).



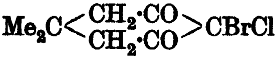
$$Me_2C<\begin{matrix}CH_2\text{——}CO\\CH_2\cdot C(OH)\end{matrix}>CCl$$

(XXV.)



$$Me_2C<\begin{matrix}CH_2\text{——}CO\\CH_2\cdot C(OBr)\end{matrix}>CCl$$

(XXVI.)

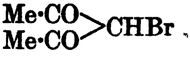


$$Me_2C<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>CBrCl$$

(XXVII.)

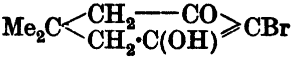
Since the compounds (XXIV) and (XXVI) are identical and both yield the same monochloro-derivative on treatment with alkali, it is evident that their formula must be represented by (XXVII), and that Vorländer's view is incorrect.

The reason why two substances so similar in structure as, for example, acetylacetone and dimethyldihydroresorcinol should behave so very differently on bromination—the one yielding a monobromo-derivative, the bromine of which is replaceable by the hydrogen of hydriodic acid, and the other a dibromo-derivative, only one of the halogen atoms of which is replaced under these conditions—must, of course, be due to the stability of the keto-form (XXVIII) in the one case and the enolic form (XXIX) in the other.*



$$\begin{matrix}Me\cdot CO\\Me\cdot CO\end{matrix}>CHBr$$

(XXVIII.)

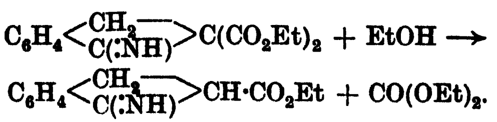


$$Me_2C<\begin{matrix}CH_2\text{——}CO\\CH_2\cdot C(OH)\end{matrix}>CBr$$

(XXIX.) *

This is, then, another instance of the *cyclo*hexane complex requiring the presence of a double bond in order to confer on it conditions of stability. Apart, however, from this, there are the more general questions regarding the mechanism of the reaction by which the reactive bromine in these compounds is replaced and the reasons which render the bromine reactive.

It is possible that bromine elimination from these compounds is determined by the tendency for the substance containing it to acquire the hydrogen atom necessary for tautomerism. The reaction may therefore be of the same kind as that which leads to the elimination of a carbethoxy-group as ethyl carbonate when esters which are potentially tautomeric are treated in alcoholic solution with a trace of sodium ethoxide. Numerous examples of this kind have now been recorded (compare Mitchell and Thorpe, T., 1910, **115**, 143; Thole and Thorpe, T., 1911, **99**, 2183, 2192; and Ingold and Thorpe, T., 1919, **115**, 143), one of the most striking being that shown by the equation:



$$C_6H_4<\begin{matrix}CH_2\text{—}\\C(:NH)\end{matrix}>C(CO_2Et)_2 + EtOH \longrightarrow$$

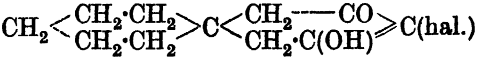
$$C_6H_4<\begin{matrix}CH_2\text{—}\\C(:NH)\end{matrix}>CH\cdot CO_2Et + CO(OEt)_2.$$

---

* Compound (XXIX) decomposes alkali carbonates.

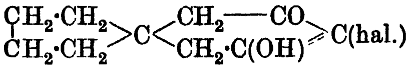
It was at first found to be impossible to convert the dihalogen derivatives of type XXXII completely into the monohalogen analogues (type XXX) by the action of aqueous sodium hydroxide, owing to the fact that the formation of sodium hypobromite led to the production of some bromoform at the expense of a carbon atom of the ring. This difficulty was ultimately overcome by carrying out the reaction in the presence of carbamide, when the change was found to be almost quantitative.

The monohalogen derivatives (XXX) and (XXXI), when hal. = Br, are readily formed by the action of excess of bromine in chloroform solution, whereas the dihalogen (dibromo) compounds (XXXII)



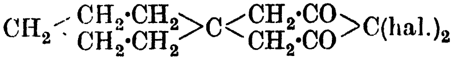
$$CH_2<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}>C<\begin{array}{l}CH_2\text{——}CO\\ CH_2\cdot C(OH)\end{array}\geqslant C(hal.)$$

(XXX.)



$$\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}>C<\begin{array}{l}CH_2\text{——}CO\\ CH_2\cdot C(OH)\end{array}\geqslant C(hal.)$$

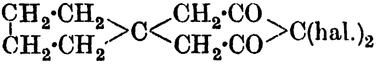
(XXXI.)



$$CH_2<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}>C<\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}>C(hal.)_2$$

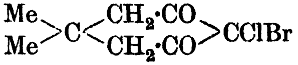
(XXXII.)

and (XXXIII) are produced only in aqueous solution. Two atoms of chlorine, however, readily enter in chloroform solution and the same ease of formation is exhibited by those dihalogen derivatives which contain both chlorine and bromine.



$$\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}>C<\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}>C(hal.)_2$$

(XXXIII.)



$$\begin{array}{l}Me\\ Me\end{array}>C<\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}>CClBr$$

(XXXIV.)

The general identity of the chlorobromo- and bromochloro-derivatives of substituted dihydroresorcinols was also proved by preparing the two types from dimethyldihydroresorcinol and showing them to have the same formula (XXXIV).

EXPERIMENTAL.

Condensation of cyclo*Hexylideneacetone with Ethyl Sodiomalonate* *Ethyl* cyclo*Hexane*spirocyclo*hexane*-3 : 5-*dione*-2-*carboxylate* (*Formula* VII, p. 1200).

The ketone was prepared by Wallach's method from *cyclo*hexanone and acetone (*Annalen*, 1912, **394**, 362); 46·5 grams were condensed with 48 grams of ethyl malonate and 7·5 grams of sodium in 150 c.c. of alcohol. After heating on the water-bath for two hours, the reaction mixture, which was now dark red, was cooled and poured into one litre of water, from which unchanged ethyl malonate was extracted by means of ether. On acidifying, an oil separated, which quickly solidified; it was obtained as small, white needles from alcohol or water and melted at 87° to a bright red liquid. It was evidently the hydrated ester containing 1 molecule of water. The yield was 84 per cent. of the theoretical (Found: $C=62\cdot30$; $H=8\cdot23$. $C_{14}H_{20}O_4,H_2O$ requires $C=62\cdot2$; $H=8\cdot2$ per cent.).

The ester behaves as a monobasic acid, dissolving with effervescence in sodium hydrogen carbonate solution, from which it is precipitated unchanged by mineral acids. Aqueous or aqueous alcoholic solutions of the ester give a reddish-violet colour with ferric chloride. On being warmed above 100° or on being dissolved in non-hydrolytic solvents, the solid ester loses its water of crystallisation. The anhydrous ester is a yellow, viscous gum which did not solidify when kept in a vacuum desiccator for several months. On exposure to moist air the anhydrous gum absorbs water and passes into the hydrated solid.

cyclo*Hexane*spirocyclo*hexane*-3 : 5-*dione* (Formula XII, p. 1200).—The acid produced on hydrolysing the ester loses carbon dioxide immediately, giving the dihydroresorcinol derivative. Hydrolysis was effected by means of baryta, 30 grams of hydrated ester being boiled under reflux for twenty hours with 100 grams of crystallised barium hydroxide and 700 grams of water. The hot solution was acidified, filtered, made strongly acid with hydrochloric acid, and boiled for fifteen minutes. On cooling, the dihydroresorcinol derivative separated in clusters of small needles.

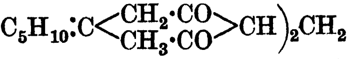
It was actually found convenient, when preparing this substance, not to isolate the ester, but to proceed directly as follows:—Fifty-six grams of ethyl malonate and 43 grams of *cyclo*hexylideneacetone were condensed by heating for two hours with a solution of 8 grams of sodium in 88 grams of alcohol. The hot solution was poured into a boiling solution containing 300 grams of crystalline barium hydroxide in 2400 grams of water and the whole boiled under reflux for twenty hours. The product was then isolated in the same way as the ester. Yield 80 per cent. of the theoretical.

cyclo*Hexane*spirocyclo*hexane*-3 : 5-*dione* behaves as a monobasic acid and dissolves in a solution of sodium hydrogen carbonate with effervescence. An aqueous alcoholic solution gives a reddish-purple colour with ferric chloride. It is readily soluble in benzene, chloroform, and alcohol, less so in water or light petroleum. It can, however, be recrystallised from any of these solvents and obtained in colourless needles which melt at 170·5° to a bright red liquid

(Found: C=73·19; H=8·87. $C_{11}H_{16}O_2$ requires C=73·3; H=8·9 per cent.).

The *anilide*, prepared as a pasty mass by boiling with aniline, was purified by rubbing with cold dilute hydrochloric acid and recrystallising from alcohol. It forms bright yellow needles which melt at 162·5° (Found: C=80·76; H=8·39; N=5·72. $C_{17}H_{21}ON$ requires C=80·0; H=8·3; N=5·5 per cent.).

*Methylenebis*cyclo*hexane*spirocyclo*hexane*-3 : 5-*dione*,



$$\left(C_5H_{10}:C\begin{matrix}<\!\!CH_2\cdot CO\!\!>\\ <\!\!CH_3\cdot CO\!\!>\end{matrix}CH\right)_2CH_2,$$

is formed as a heavy, white precipitate upon adding formaldehyde solution to a warm aqueous solution of the dihydroresorcinol derivative. It forms short, colourless needles from alcohol and melts at 206° (Found: C=73·61; H=8·65. $C_{23}H_{32}O_4$ requires C=74·1; H=8·7 per cent.).

Oxidation of cyclo*hexane*spirocyclo*hexanedione to* cyclo*hexane*-1 : 1-*diacetic acid* (formula XVII, p. 1201) was effected by means of bromine and sodium hydroxide. Five grams, dissolved in 25 c.c. of 10 per cent. sodium hydroxide solution and cooled to 0°, were slowly added, with vigorous shaking, to an ice-cold solution of 15·5 grams of bromine in 350 c.c. of water which had been neutralised with 10 per cent. sodium hydroxide solution. After standing in ice for thirty minutes, a test portion no longer gave a precipitate with hydrochloric acid. A slight excess of sodium sulphite solution was now added and the filtered solution acidified with hydrochloric acid. A quantitative yield of *cyclo*hexanediacetic acid, melting at 179°, was obtained on extracting with ether (Found: C=60·23; H=8·07. Calc., C=60·0; H=8·1 per cent.).

Oxidation to cyclo*Hexane*-1-*acetic*-1-*carboxylic Acid* (Formula XVIII, p. 1202).—Four grams were dissolved in 10 c.c. of 10 per cent. sodium hydroxide solution and 13 grams of potassium permanganate dissolved in cold water were added. The mixture was allowed to stand at room temperature for forty-eight hours, when the excess of permanganate was destroyed by sulphur dioxide and the acidified liquid extracted with ether. The pure acid forms colourless prisms from water and melts at 134° (Found: C=57·94; H=7·65. $C_9H_{14}O_4$ requires C=58·0; H=7·6 per cent.).

The *silver* salt is obtained as a colourless precipitate (Found: Ag=53·96. $C_9H_{12}O_4Ag_2$ requires Ag=53·9 per cent.).

The *anhydride*, prepared by boiling the acid with acetyl chloride for one and a half hours, crystallises well from light petroleum (b. p. 40—60°) as colourless glistening plates which melt at 57° (Found: C=64·19; H=7·23. $C_9H_{12}O_3$ requires C=64·2; H=7·2 per cent.).

The *anilic acid*, prepared from the anhydride and aniline in benzene solution, crystallises from alcohol as glistening plates which soften at 176° and melt with evolution of steam at 180° (Found: C = 68·96; H=7·78. $C_{15}H_{19}O_3N$ requires C=68·9; H=7·3 per cent.).

*cyclo*Hexane-1-acetic-1-carboxylic acid is characterised by forming a calcium salt, which is precipitated on boiling a neutral solution of the ammonium salt containing calcium chloride.

Condensation of cyclo*Pentylideneacetone with Ethyl Sodiomalonate. Ethyl* cyclo*Pentane*spirocyclo*hexane-3 : 5-dione-2-carboxylate* (*Formula* VIII, p. 1200).

The ketone was prepared by the dry distillation of the calcium salt of *cyclo*pentane-1 : 1-diacetic acid in a current of nitrogen (Kon, this vol., p. 822). The condensation was effected in the same manner as in the previous experiment and the product isolated in the same way. The solid (hydrated) ester can be recrystallised from dilute alcohol if a solution in this solvent saturated at 55° is allowed to cool after having been seeded, but the operation is a difficult one owing to the ready manner in which the substance loses its water of hydration. It forms, in its hydrated condition, small, colourless plates which melt at 65—67°, forming a red liquid. It can also be recrystallised from dilute acetic acid (Found: C=60·63; H=7·80. $C_{13}H_{18}O_2,H_2O$ requires C=60·9; H=7·9 per cent.).

The anhydrous ester, which is readily formed when an ether solution of the hydrated modification is dried with calcium chloride, is obtained as a yellow oil on evaporating the ether. It is a monobasic acid which decomposes solutions of sodium hydrogen carbonate, and gives a reddish-purple colour in alcoholic solution with ferric chloride.

cyclo*Pentane*spirocyclo*hexane*-3 : 5-*dione* (Formula XIII, p. 1200).—Hydrolysis of the above ester may be effected by barium hydroxide solution, or the dihydroresorcinol derivative may be prepared without isolating the ester. In both cases the operations are the same as those described in the case of the higher homologue. The yield by the direct process was 80 per cent. of the theoretical.

The diketone separates from benzene as colourless needles melting to a red liquid at 135—136·5°; it is soluble in chloroform, benzene, and alcohol, and gives in alcoholic solution a reddish-purple colour with ferric chloride (Found: C=71·74; H=8·47. $C_{10}H_{14}O_2$ requires C=72·2; H=8·5 per cent.).

The *anilide* was prepared by boiling with excess of aniline for five minutes. After purification in the usual manner, it forms clusters of bright yellow needles from alcohol and melts at 171° (Found: N=6·10. $C_{16}H_{19}ON$ requires N=5·9 per cent.).

*Methylenebis*cyclo*pentane*spirocyclo*hexane-3 : 5-dione* is obtained by the action of formaldehyde solution on an aqueous solution of the diketone. It forms flattened needles from alcohol and melts at 165° (Found: C=73·23; H=8·17. $C_{21}H_{28}O_4$ requires C=73·2; H=8·2 per cent.).

Oxidation of the diketone to cyclo*pentane-*1 : 1*-diacetic acid* (formula XIX, p. 1202), was carried out in the same way as described on page 1206, 1 gram of the *spiro*-compound, dissolved in 10 c.c. of 10 per cent. sodium hydroxide solution, being treated with 3·4 grams of bromine in 100 c.c. of water. The yield of the diacetic acid (m. p. 178—179°) was quantitative (Found: C=57·68; H=7·50. Calc., C=58·0; H=7·6 per cent.).

Oxidation to cyclo*Pentane-*1*-acetic-*1*-carboxylic Acid* (Formula XX, p. 1202).—Six hundred c.c. of 1·5 per cent. aqueous permanganate were slowly added at room temperature to 2 grams of the *spiro*-compound and 5 grams of sodium carbonate dissolved in 160 c.c. of water. The product, worked up in the usual way, gave 1 gram of crystalline acid, which formed short colourless needles from alcohol and melted at 156·5° (Found: C=55·98; H=6·94. $C_8H_{12}O_4$ requires C=55·8; H=7·0 per cent.).

Condensation of Ethyl cyclo*Hexylideneacetate with Ethyl Sodiocyanoacetate. Production of* cyclo*Hexane-*1 : 1*-diacetic Acid.*

*cyclo*Hexylideneacetic acid was prepared by the method of Beesley, Ingold, and Thorpe (T., 1915, **107**, 1099) and esterified. The neutral ester (10·5 grams) was then condensed with the sodium compound of ethyl cyanoacetate formed by mixing 8 grams of ethyl cyanoacetate with a solution containing 1·6 grams of sodium dissolved in 80 grams of alcohol; the reaction was finished after heating for two hours on the water-bath. The condensation product was then extracted in the usual way and hydrolysed, without further purification, by boiling with 50 per cent. aqueous sulphuric acid for four hours. The product yielded white crystals of the diacetic acid, which melted at 178—180° and showed no depression of the melting point when mixed with a specimen of the pure acid.

The Halogen Derivatives of cyclo*Hexane*spirocyclo*hexane-3 : 5-dione.*

cyclo*Hexane*spiro-4-*bromo*cyclo*hexane-3 : 5-dione* (*Formula* XXX, p. 1204).

Slight excess of bromine dissolved in chloroform was added gradually, with shaking, to a chloroform solution of the dihydroresorcinol derivative. After the solvent had been evaporated on the water-bath a syrup remained, from which the solid bromo-derivative was obtained by solution in chloroform and addition of light petroleum. It was found necessary, in order to remove traces of a more highly brominated product, to boil the solid for ten minutes with a 10 per cent. solution of alkali hydroxide, and to recrystallise the bromo-compound, reprecipitated by acid, from benzene. It forms colourless needles melting at 177° (Found: Br=30·69. $C_{11}H_{15}O_2Br$ requires Br=30·8 per cent.). The bromo-derivative dissolves in aqueous solutions of alkali carbonates and alkali hydroxides.

cyclo*Hexane*spiro-4 : 4-*dibromo*cyclo*hexane*-3 : 5-*dione* (Formula XXXII, p. 1204).—Two grams of the dihydroresorcinol derivative were added to 20 c.c. of water containing 10 grams of bromine and the whole was ground together in a mortar. The yellow, granular solid formed in this way was purified by first grinding it with sodium hydrogen carbonate solution and then recrystallising it from benzene or dilute alcohol. It forms long, colourless needles which melt at 125° (Found: Br=46·90. $C_{11}H_{14}O_2Br_2$ requires Br=47·1 per cent.).

The conversion of the dibromo-derivative into the monobromo-compound can be almost quantitatively effected by treating 1 gram with 20 c.c. of a 10 per cent. solution of sodium hydroxide containing excess of carbamide. The dibromo-derivative passes into solution with rise of temperature, and at the same time nitrogen is evolved. The clear solution yields 0·74 gram of the monobromo-derivative on acidification.

cyclo*Hexane*spiro-4-*chloro*cyclo*hexane*-3 : 5-*dione* (Formula XXX, p. 1204).—Slight excess of dry chlorine gas was passed into a chloroform solution of the *spiro*-compound and the solvent evaporated. The residue was then treated with sodium hydrogen carbonate solution and the monochloro-derivative precipitated from the filtrate by hydrochloric acid. It forms colourless needles from alcohol and melts at 166·5° (Found: C=61·36; H=6·90. $C_{11}H_{15}O_2Cl$ requires C=61·5; H=7·0 per cent.).

The compound combines with one molecule of water of crystallisation, which it loses in an evacuated desiccator. It gives a reddish-purple coloration with ferric chloride.

cyclo*Hexane*spiro-4 : 4-*dichloro*cyclo*hexane*-3 : 5-*dione* (Formula XXXII, p. 1204) is the insoluble residue left after treatment with sodium hydrogen carbonate solution in the above experiment, and can also be obtained in quantitative yield if a large excess of chlorine is used. It crystallises from alcohol as colourless needles which melt at 89° (Found: C=53·04; H=5·79. $C_{11}H_{14}O_2Cl_2$ requires C=53·0; H=5·7 per cent.).

The dichloro-derivative is completely converted into the monochloro-compound by treatment with potassium iodide in glacial acetic acid solution.

cyclo*Hexane*spiro-4-*chloro*-4-*bromo*cyclo*hexane*-3 : 5-*dione* (Formula XXXII, p. 1204) can be prepared either by treating the monobromo-derivative with chlorine or from the monochloro-derivative on treatment with bromine, both operations being carried out in chloroform solution and the product being freed from any unchanged monohalogen compound by treatment with sodium hydrogen carbonate solution. It forms slender colourless needles from light petroleum (b. p. 60—70°) and melts at 101° (Found: C=45·34; H=4·90. $C_{11}H_{14}O_2ClBr$ requires C=45·0; H=4·8 per cent.).

The compound is converted into the monochloro-derivative on treatment with an aqueous solution of sodium hydroxide and carbamide.

4-*Chloro*-4-*bromo*-1 : 1-*dimethyl*cyclo*hexane*-3 : 5-*dione* (Formula XXXIV, p. 1204) is prepared either by the chlorination of the monobromo-derivative (Vorländer, *Annalen*, 1902, **322**, 239) or by the bromination of the monochloro-derivative (Vorländer, *loc. cit.*), in chloroform solution. It separates from light petroleum (b. p. 60—80°) as long, felted, colourless needles which melt at 138·5° (Found: C=37·76; H=4·03. $C_8H_{10}O_2ClBr$ requires C=37·9; H=4·0 per cent.).

The compound is converted into the monochloro-derivative (m. p. 161°) by means of potassium hydroxide solution and carbamide.

cyclo*Pentane*spiro-4-*bromo*cyclo*hexane*-3 : 5-*dione* (Formula XXXI, p. 1204), prepared in the same manner as the *cyclo*hexane homologue, separates from alcohol as flat, colourless plates which melt at 157° (Found: Br=32·62. $C_{10}H_{13}O_2Br$ requires Br=32·6 per cent.).

cyclo*Pentane*spiro-4 : 4-*dibromo*cyclo*hexane*-3 : 5-*dione* (Formula XXXIII, p. 1204) is the material formed in the above experiment which is insoluble in sodium hydrogen carbonate solution. It crystallises from benzene as needles and melts at 111° (Found: Br=48·21. $C_{10}H_{12}O_2Br_2$ requires Br=47·6 per cent.).

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CXXXV.—*Dyes derived from Phenanthraquinone.*

By EDWIN ROY WATSON and SIKHIBHUSHAN DUTT.

THIS work was started in the British Dyes laboratory at the Leeds University in 1918 with the object of preparing valuable dyes from phenanthrene. Most of the new compounds described were again prepared in the Dacca College laboratory, and all the recorded analyses were made there. The investigation is to some extent a continuation of that described in T., 1916, **109**, 617. It may conveniently be divided into four parts.

(A) *Attempts to Prepare the Phenanthraquinone Analogues of the Anthracene Mordant Dyes.*

Mention has already been made (*loc. cit.*) of the interesting dyeing properties of 3 : 4-dihydroxyphenanthraquinone (morpholquinone). Dr. Barger kindly gave one of us a small sample of 3 : 4-dihydroxyphenanthrene, from which we were able to prepare morpholquinone and to test the fastness of its dyeings, which were found to be excellent in all respects. Renewed efforts were made to obtain dyes of this class by the methods used in the anthracene series. It seemed possible that the failure to produce anything of interest by the action of fuming sulphuric acid and sulphur on 2 : 7-dinitrophenanthraquinone (*loc. cit.*) was due to the unfavourable position of the nitro-groups, as the *para*-positions to these groups are not free. Similar experiments were therefore carried out with 4 : 5-dinitrophenanthraquinone, but with no better success. Attempts were also made to convert the nitro-groups into hydroxylamino-groups by other methods, with the idea of then inducing the hydroxyl groups to wander and produce the diaminodihydroxy-compound. But attempts at reduction with zinc dust and ammonium chloride, zinc dust and dilute acid, sodium stannite, sodium sulphide, electrolytic reduction, and reduction to the amino-compound followed by diazotisation and treatment with hydroxylamine (compare Wacker, *Ber.*, 1902, **35**, 3927) were equally unsuccessful. It was possible that the failure to produce interesting dyes by the action of manganese dioxide and sulphuric acid on 2-hydroxy- and 2 : 7-dihydroxy-phenanthraquinone was due to the unfavourable position of the hydroxyl groups and that better results might be obtained by the action of oxidising agents on phenanthraquinone derivatives with the auxochrome in the

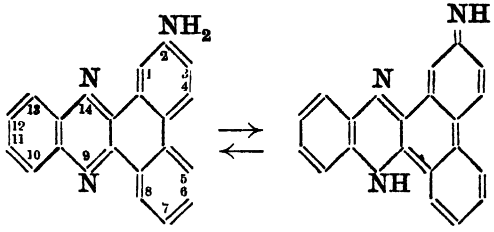
3-position. But neither manganese dioxide and sulphuric acid nor persulphate and sulphuric acid gave any interesting product with 3-aminophenanthraquinone. The action of persulphate on phenanthraquinone itself was equally unsuccessful.

(B) *Attempts to Prepare Phenanthraquinone Vat Dyes.*

Further attempts to use the compounds already described (*loc. cit.*), for example, 2-benzoylamino- and 2 : 7-dibenzoyldiaminophenanthraquinone, by modification of the dyeing vat led to no better results. Attempts were made to produce phenanthraquinone-imides by condensing together (*a*) 2-aminophenanthraquinone (2 mols.) and dibromophenanthraquinone (1 mol.) (D.R.-P. 222206), (*b*) 4 : 5-diaminophenanthraquinone (1 mol.) and the same dibromo-compound (1 mol.), (*c*) 3-amino- and 3-bromo-phenanthraquinone (1 mol. of each). The substances were boiled together in nitrobenzene or naphthalene solution with fused sodium acetate and with or without cuprous chloride, but the dark brown products were insoluble in hyposulphite. The phenanthraquinone molecules were probably destroyed by the treatment. Skraup's reaction applied to phenanthraquinone gave no definite product (compare the preparation of Indanthrene Dark Blue B.O.).

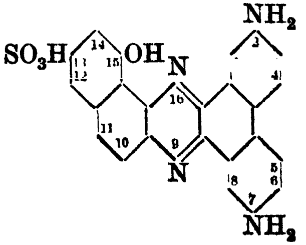
(C) *Preparation of Azine Derivatives of Phenanthrene.*

One of the best known reactions of phenanthraquinone is its condensation with *o*-diamines to form phenanthrazines. With (T., 1886, **49**, 401) prepared a dyestuff (a new eurhodine, as he termed it) by the action of 1 : 2 : 4-triaminobenzene on phenanthraquinone, but its dyeing properties were not good. He also prepared a hydroxyphenanthranaphthazine (eurhodol) (*Ber.*, 1886, **19**, 2793), but its dyeing properties and those of its sulphonic acid were also unsatisfactory. According to D.R.-P. 90212 and 90213, yellow wool dyes of good fastness are obtained by condensing phenanthraquinone with such compounds as 7 : 8-diamino-1-naphthol-3-sulphonic acid or by condensing the quinone with 1 : 2-diaminonaphthalenedisulphonic acids and fusing the products with alkalis, the dyestuffs formed being phenanthranaphthazines with a hydroxyl group in the *peri*-position to one of the azine nitrogen atoms. But these products do not appear to have been put on the market. It was thought that, if phenanthraphenazines could be prepared with auxochromes in the phenanthrene nucleus, they would be deep-coloured dyes, as they would be quinonoid in all possible tautomeric forms and would have long chains of conjugate linkings (see Watson, T., 1914, **105**, 759; Watson and Meek, T., 1915, **107**, 1567), for example, 2-aminophenanthraphenazine,



2-Amino-, *3-amino-*, *4-amino-*, *2 : 7-diamino-*, *and 4 : 5-diaminophenanthraphenazine* have been prepared by condensing the corresponding amino-derivatives of phenanthraquinone with *o*-phenylenediamine. But contrary to expectation, they are all yellow and dye light shades on wool. Interesting but unexpected relations between colour and constitution were encountered on reducing 2 : 7-dinitrophenanthraphenazine. There was obtained *2 : 7-diaminodihydrophenanthraphenazine*, which is a violet base forming a yellow *hydrochloride* and a yellow *acetyl* derivative. It dyes yellow shades on wool, but its dyeing properties are unsatisfactory. On diazotisation and boiling with water, it gives 2 : 7-dihydroxydihydrophenanthraphenazine, which is brown and only slightly soluble in alkalis.

Phenanthrazine dyes were also prepared containing auxochromes on both sides of the molecule, for example, *2 : 7 : 11-triaminophenanthraphenazine*, by condensing 2 : 7-diaminophenanthraquinone and 1 : 2 : 4-triaminobenzene. The base is yellowish-brown, it forms magenta-coloured salts and dyes moderately fast yellow shades on wool. *2 : 7-Diamino-15-hydroxyphenanthranaphthazine-13-sulphonic acid*,



was prepared from 2 : 7-diaminophenanthraquinone and 7 : 8-diamino-1-naphthol-3-sulphonic acid. It dyes only yellow shades, but the dyeings are very fast to all agencies. The corresponding *2 : 7-dinitro-15-hydroxyphenanthranaphthazine-13-sulphonic acid*, prepared from 2 : 7-dinitrophenanthraquinone in the same way, dyes bright orange-yellow shades on wool.

The fact that diaminodihydrophenanthraphenazine has a deeper colour than diaminophenanthraphenazine directed attention to the flavinduline group of dyes, which may be regarded as phenanthraphenazines with alkyl or aryl haloid added to one of the azine nitrogen atoms. Flavinduline itself is yellow, but dyes of all colours can be obtained by condensing phenanthraquinone with substituted *o*-diamines such as amidodiphenyl-*m*-phenylenediamine, 4-methylamino-2 : 5-tolylenediamine, 4-methylamino-*m*-toluidine, etc. (D.R.-P. 79570). The great effect of additional auxochromes in the benzene nucleus on the depth of colour of dyes of this group made it appear worth while to study the effect of additional auxochromes on the phenanthrene side of the molecule. 2-Amino- and 2 : 7-diamino-flavinduline, in which the amino-groups are in the phenanthrene part of the molecule, have been prepared (*Ber.*, 1899, **32**, 2634). Diaminoflavinduline hydrobromide was described as forming blackish-green crystals and dissolving in water or alcohol with a yellowish-green colour, but its dyeing properties were not tested. The corresponding 2 : 7-*dinitro*- and 2 : 7-*diamino*-11 : 4′-*dimethylflavindulines* have now been prepared and their dyeing properties tested. They are comparatively unstable substances and the dyeing properties of the diamino-compound are not interesting. It gives dirty brownish-green shades.

(D) *Miscellaneous.*

On account of its deep colour, Mukherjee and Watson (*loc. cit.*) made some attempts to use 2 : 7-diaminophenanthraquinone as a dye. Schmidt had previously recorded (*Ber.*, 1903, **36**, 3749) that 4 : 5-diaminophenanthraquinol hydrochloride dyes wool from an acid bath and on after-oxidation gives olive-brown shades which are relatively fast to alkalis and washing, but possess no interest for practical purposes because of their slight fastness to rubbing. It has now been found that 2 : 7-diaminophenanthraquinol hydrochloride dyes similar shades (probably in both cases due to the combination of the diamino-quinone with the fibre), that dark brown, almost black, dyeings are obtained with 2 per cent. dyestuff, and that the dyeings can be rendered fast to rubbing by washing with soap and warm water (gentle neutral milling). Similar but somewhat lighter dyeings can be obtained with the corresponding 2-amino- and 4-amino-compounds.

Azo-dyes can be prepared from a number of the phenanthrene derivatives already described. The following have been prepared: *phenanthraquinone*-2 : 7-*bisazonaphthionic acid*, *phenanthraquinone*-2 : 7-*bis*-(2′)-*azo*-7′-*amino*-1′-*hydroxynaphthalene*-3′-*sulphonic acid*, *phenanthraquinone*-4 : *5-bis-(2′)-azo-7′-amino-1′-hydroxynaphthalene-3′-sulphonic acid, dihydrophenanthraphenazine*-2 : *7-bisazonaphthionic acid*, and 11-*aminophenanthraphenazine*-2 : 7-*bis*-(2′)-*azo*-7′-*amino*-1′-*hydroxynaphthalene*-3′-*sulphonic acid*. The 2 : 7-phenanthraquinone derivatives are good direct cotton dyes, but probably no better than the corresponding dyes from benzidine. The 4 : 5-phenanthraquinone derivatives have little affinity for cotton, but are good wool dyes. The other two dyes have no specially valuable properties.

The preparation of dyes from phenanthraquinone and aromatic hydrazinesulphonic acids was described in D.R.-P. 40745 of 1887. The products were described as acid wool dyes fast to acids and alkalis. 2 : 7-*Diaminophenanthraquinonediphenylhydrazone*-pp′ *disulphonic acid* has now been prepared by the condensation of 2 : 7-diaminophenanthraquinone and phenylhydrazine-*p*-sulphonic acid. It is an acid wool dye soluble in alkalis, but its dyeings are not particularly fast.

EXPERIMENTAL.

2-*Aminophenanthraphenazine*, $NH_2\cdot C_{14}H_7{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6H_4$.

2-Aminophenanthraquinone (3 grams) and *o*-phenylenediamine (1·5 grams) were mixed together with 20 c.c. of alcohol and heated on the water-bath under reflux for three hours. The yellow, crystalline mass that separated was dissolved in hot pyridine and after the cautious addition of hot water was deposited on cooling as yellow, prismatic needles. It melts at 220—221° and is sparingly soluble in acetic acid and alcohol and insoluble in water. It dyes wool to bright yellow shades from a 5 per cent. acetic acid bath (Found : N=14·4. $C_{20}H_{13}N_3$ requires N=14·2 per cent.).

4-*Aminophenanthraphenazine*, $NH_2\cdot C_{14}H_7{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6H_4$.

This substance was prepared from 4-aminophenanthraquinone in the same way as the preceding one was obtained from the 2-aminoquinone. It was obtained as dull yellow needles from pyridine, melted above 285°, and in its other properties resembled the preceding compound (Found : N=13·9. $C_{20}H_{13}N_3$ requires N=14·2 per cent.).

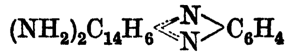
2 : 7-*Diaminophenanthraphenazine*, $(NH_2)_2C_{14}H_6{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6H_4$.

2 : 7-Diaminophenanthraquinone (2·4 grams) and *o*-phenylenediamine (1·3 grams) were boiled with 50 c.c. of glacial acetic acid for two hours under reflux. The dark colour of the amino-quinone rapidly

disappeared and a precipitate of bright yellow needle-shaped crystals was obtained. An equal volume of water was added and the mixture cooled. The precipitate was crystallised from pyridine and water and obtained in brilliant yellow needles.

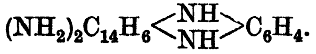
The substance is slightly soluble in alcohol and ether, more soluble in acetic acid, and very soluble in pyridine, aniline, and nitrobenzene. It dyes light yellow shades on wool (Found: N=18·2. $C_{20}H_{14}N_4$ requires N=18·1 per cent.).

Treatment with hydrochloric acid and stannous chloride gives an immediate violet colour similar to that obtained by reducing the corresponding dinitrophenanthraphenazine with tin and hydrochloric acid.



4 : 5-*Diaminophenanthraphenazine*, $(NH_2)_2C_{14}H_6{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6H_4$, was prepared in a similar way to the preceding compound and has similar properties.

2 : 7-*Diaminodihydrophenanthraphenazine*,



$$(NH_2)_2C_{14}H_6{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C_6H_4.$$

One part of 2 : 7-dinitrophenanthraphenazine (*Ber.*, 1903, **36**, 3738) was made into a paste with 15 parts of concentrated hydrochloric acid, treated with 2 parts of tin, and warmed on the water-bath for a few hours. The tin disappeared and brownish-purple, needle-shaped crystals were produced. These were filtered off, washed with concentrated hydrochloric acid, and dried on porous porcelain. They were then boiled with sodium acetate or sodium carbonate solution and the insoluble product was filtered off, dried, and extracted with pyridine. On dilution, the pyridine solution deposited the base in beautiful violet needles. The substance is soluble in pyridine, aniline, or nitrobenzene, but only sparingly soluble in alcohol or acetic acid. It does not melt below 280° (Found: N=17·6, 17·9. $C_{20}H_{16}N_4$ requires N=17·9 per cent.).

2 : 7-*Diaminodihydrophenanthraphenazine hydrochloride*,

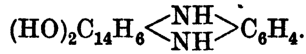
$$(NH_2)_2C_{14}H_6{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C_6H_4,4HCl,$$

was prepared by warming the base with a little concentrated hydrochloric acid, when it was changed into a yellow solid, which was filtered off, washed with a little concentrated hydrochloric acid and dried on porous porcelain in a vacuum (Found: Cl=31·2. $C_{20}H_{16}N_4,4HCl$ requires Cl=31·0 per cent.).

The hydrochloride dissolves in warm water or dilute hydrochloric acid. Sodium acetate or carbonate precipitates the base from these solutions as a red precipitate which becomes violet on boiling. The aqueous solution of the hydrochloride at first dyes wool yellow, but on warming the bath the free base is deposited in the bath and the dyeings are unsatisfactory.

The *tetra-acetyl* derivative of 2 : 7-diaminodihydrophenanthraphenazine, $\mathrm{(NHAc)_2C_{14}H_6}\genfrac{<}{>}{0pt}{}{\mathrm{NAc}}{\mathrm{NAc}}\mathrm{C_6H_4}$ or $\mathrm{(NAc_2)_2C_{14}H_6}\genfrac{<}{>}{0pt}{}{\mathrm{NH}}{\mathrm{NH}}\mathrm{C_6H_4}$, was obtained as a yellow, crystalline substance by treating the base with acetic anhydride and a trace of pyridine. Clusters of needles were obtained by recrystallising from alcohol. It does not melt below 285° (Found: $N=11\cdot4$. $C_{28}H_{24}O_4N_4$ requires $N=11\cdot7$ per cent.).

2 : 7-*Dihydroxydihydrophenanthraphenazine*,



$$\mathrm{(HO)_2C_{14}H_6}\genfrac{<}{>}{0pt}{}{\mathrm{NH}}{\mathrm{NH}}\mathrm{C_6H_4}.$$

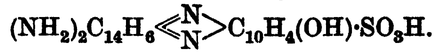
The corresponding diamino-hydrochloride described above was dissolved in water and diazotised with 2 molecules of sodium nitrite, when a dark red solution was obtained. This was filtered and boiled, when the dihydroxy-compound was precipitated in dark brown flocks. It was obtained crystalline (as minute brownish-yellow needles which do not melt below 280°) from a mixture of equal parts of nitrobenzene and glacial acetic acid, and is also soluble in aniline. It becomes darker in colour on adding alkalis, but does not dissolve completely (Found: $N=9\cdot2$. $C_{20}H_{14}O_2N_2$ requires $N=8\cdot9$ per cent.).

2:7:11-*Triaminophenanthraphenazine*, $\mathrm{(NH_2)_2C_{14}H_6}\genfrac{<}{>}{0pt}{}{\mathrm{N}}{\mathrm{N}}\mathrm{C_6H_3{\cdot}NH_2}$.

2 : 7-Diaminophenanthraquinone (1·2 grams) and 1 : 2 : 4-triaminobenzene hydrochloride (1 gram) were boiled with 20 c.c. of water for half an hour under reflux. Forty c.c. of water were then added and the boiling was continued for another half hour. A dark violet solution was obtained, which was filtered and treated with excess of sodium acetate, the base being thereby precipitated as a brown, gelatinous mass. This was recrystallised from dilute pyridine and obtained as yellowish-brown, prismatic needles. It does not melt below 280° (Found: $N=21\cdot7$. $C_{20}H_{15}N_5$ requires $N=21\cdot5$ per cent.).

The condensation can also be brought about in glacial acetic acid. The *hydrochloride* can be obtained by dissolving the base in a little hot, dilute hydrochloric acid, cooling the violet solution, and adding excess of concentrated hydrochloric acid, which gives a violet precipitate of the hydrochloride. It dyes strong yellow shades on wool (full shade with 1 per cent.).

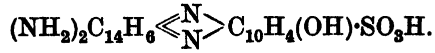
2 : 7-*Diamino*-15-*hydroxyphenanthranaphthazine*-13-*sulphonic Acid*,



$$(NH_2)_2C_{14}H_6{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_{10}H_4(OH)\cdot SO_3H.$$

This compound was prepared by boiling 2 : 7-diaminophenanthraquinone and 7 : 8-diamino-1-naphthol-3-sulphonic acid in equimolecular proportions with a little water under reflux. The dark aminoquinone quickly disappeared and a yellowish-brown solid was formed. This was filtered off, dissolved in dilute potassium hydroxide solution, filtered and reprecipitated by dilute acid as bright yellow flocks, which could not be crystallised. It dyes yellow shades on wool (Found: N=12·7, 12·8. $C_{24}H_{16}O_4N_4S$ requires N=12·3 per cent.).

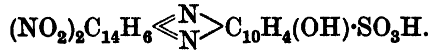
4 : 5-*Diamino*-15-*hydroxyphenanthranaphthazine*-13-*sulphonic Acid*,



$$(NH_2)_2C_{14}H_6{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_{10}H_4(OH)\cdot SO_3H.$$

This compound was prepared in a similar way from 4 : 5-diaminophenanthraquinone and has similar properties to the preceding compound (Found: N=12·1. $C_{24}H_{16}O_4N_4S$ requires N=12·3 per cent.).

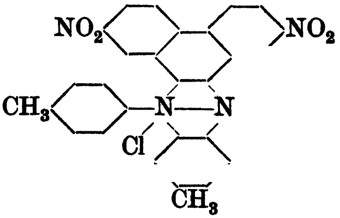
2 : 7-*Dinitro*-15-*hydroxyphenanthranaphthazine*-13-*sulphonic Acid*,



$$(NO_2)_2C_{14}H_6{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_{10}H_4(OH)\cdot SO_3H.$$

This acid was prepared in a similar way from 2 : 7-dinitrophenanthraquinone and the same diaminonaphtholsulphonic acid. A fox-red colour was soon produced and the solids dissolved almost completely. The dyestuff was salted out. When isolated, it was found to be not very soluble in water.

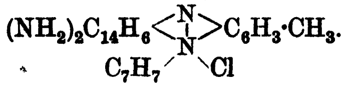
2 : 7-*Dinitro*-11 : 4′-*dimethylflavinduline Chloride*,



2 : 7-Dinitrophenanthraquinone (2·9 grams) was dissolved in 250 c.c. of hot glacial acetic acid and cooled to 50°. A solution of 2·2 grams of *o*-amino-di-*p*-tolylamine in 20 c.c. of glacial acetic acid

and 5 c.c. of concentrated hydrochloric acid was gradually added and caused the rapid precipitation of bright golden-yellow needles of the new substance. After two days the crystals were filtered off and dried in a vacuum desiccator. They are easily decomposed, for example, on attempting to crystallise from acetic acid or to dry in the steam-oven (Found: Cl=7·3. $C_{28}H_{19}O_4N_4Cl$ requires Cl=7·0 per cent.).

2 : 7-*Diamino*-11 : 4′-*dimethylflavinduline Chloride*,



$$(NH_2)_2C_{14}H_6{<}\overset{N}{\underset{\underset{C_7H_7\diagup\quad\diagdown Cl}{N}}{|}}{>}C_6H_3{\cdot}CH_3.$$

2 : 7-Diaminophenanthraquinone (1 gram) was obtained in a finely divided condition by solution in pyridine and precipitation with water. It was filtered off, washed with water, pressed as far as possible free from water and mixed with *o*-amino-di-*p*-tolylamine (1 gram), 10 c.c. of glacial acetic acid, and 2 c.c. of concentrated hydrochloric acid. The mixture was thoroughly triturated and allowed to stand for three days. A dark brown, amorphous powder was formed, which was filtered off after the addition of 10 c.c. of water, washed with a little water, and dried in a vacuum at the ordinary temperature. It is somewhat soluble in water and decomposes in the steam-oven.

This substance could also be obtained by the reduction of the preceding dinitro-compound, but owing to its instability the direct preparation from the diamino-quinone is preferable. It was not obtained crystalline (Found: Cl=8·2. $C_{28}H_{23}N_4Cl$ requires Cl=7·9 per cent.).

Phenanthraquinone-2 : 7-*bis*-(2′)-*azo*-7′-*amino*-1′-*hydroxynaphthalene*-3′-*sulphonic Acid*, $C_{14}H_6O_2[N_2{\cdot}C_{10}H_4(NH_2)(OH){\cdot}SO_3H]_2$.

2 : 7-Diaminophenanthraquinone (1 gram) was diazotised in the usual way by suspending in cold dilute sulphuric acid (5 per cent.) and adding sodium nitrite (0·51 gram; 2 mols.). The quinone dissolved and, after thorough stirring, the solution was filtered and poured into a solution of 2·2 grams of 7-amino-1-naphthol-3-sulphonic- acid (γ-acid) (5 per cent. more than the theoretical quantity) in excess of dilute sodium hydroxide. Immediately the colour of the solution changed to deep violet. It was thoroughly stirred for two hours and then kept for two days, when it was filtered, exactly neutralised by dilute hydrochloric acid, evaporated to a small volume, and acidified with hydrochloric acid. The dye, which was precipitated in dark violet flocks, was filtered off, washed

with water (although with considerable loss) and alcohol and dried in the steam-oven. It is a dark violet, amorphous powder, very readily soluble in water and sparingly soluble in alcohol or acetic acid (Found : N=11·9. $C_{34}H_{22}O_{10}N_6S_2$ requires N=11·4 per cent.).

The dyestuff in the form of sodium salt is a typical direct cotton dye, dyeing more violet (less blue) shades than Diamine Black R.O. It is not a good union dye, as it has more affinity for cotton than for wool when dyed from a neutral bath with 10 per cent. sodium chloride at 50°, 75°, or 100°.

Phenanthraquinone-4 : 5-bis-(2′)-azo-7′-amino-1′-hydroxynaphthalene-3′-sulphonic Acid, $C_{14}H_6O_2[N_2\cdot C_{10}H_4(NH_2)(OH)\cdot SO_3H]_2$.

This compound was prepared in a similar way to the preceding dyestuff (Found : N=11·7. $C_{34}H_{22}O_{10}N_6S_2$ requires N=11·4 per cent.).

The dyestuff in the form of sodium salt does not give such strong dyeings on cotton as the corresponding 2 : 7-derivative and the vat is not exhausted. It dyes good reddish-violet shades on wool from an acid bath.

Dihydrophenanthraphenazine-2 : 7-bis-(2′)-azonaphthionic Acid, $C_{20}H_{12}N_2[N_2\cdot C_{10}H_5(NH_2)\cdot SO_3H]_2$.

2 : 7-Diaminodihydrophenanthraphenazine was diazotised as already described in the preparation of the corresponding dihydroxy-compound. The diazo-solution was then added to a cold solution of sodium naphthionate (2 mols.) in sodium carbonate, when the dyestuff was at once precipitated in rhombohedral crystals. For analysis, the free acid was obtained by treating the dye with hydrochloric acid. It is almost insoluble in water and organic solvents (Found : N=14·4. $C_{40}H_{28}O_6N_8S_2$ requires N=14·4 per cent.).

It is a direct cotton dye giving reddish-violet shades, but the fastness of the dyeings to acid and alkali is no better than that of benzopurpurin 4B.

11-Aminophenanthraphenazine-2 : 7-bis-(2′)-azo-7′-amino-1′-hydroxynaphthalene-3′-sulphonic Acid, $NH_2\cdot C_{20}H_9N_2[N_2\cdot C_{10}H_4(NH_2)(OH)\cdot SO_3H]_2$.

Triaminophenanthraphenazine (1 gram) was treated in the cold with excess of dilute hydrochloric acid and 3 molecules of sodium nitrite, the latter causing the disappearance of the violet colour of the hydrochloride and producing a yellowish-brown solution, which was filtered into a solution of 2·1 grams of γ-acid in excess of dilute sodium hydroxide. An immediate violet coloration was produced and some precipitate was deposited. After standing for two days, the mixture was heated at 60° for three hours and the precipitate was filtered off, washed, heated with hydrochloric acid, and again filtered off and washed. It was thus obtained as a violet, amorphous powder, moderately soluble in water or alcohol, which left no ash on ignition (Found: N=16·6, 15·3, 15·8, 15·1. $C_{40}H_{27}O_8N_9S_2$ requires N=15·2 per cent.).

Attempts to estimate sulphur were unsuccessful, as the dye was not completely decomposed by heating in a sealed tube with fuming nitric acid at 260° for eight hours, opening the tube, again closing, and heating for sixteen hours at 260°, but the nitrogen estimations indicate that only two of the amino-groups of triaminophenanthraphenazine have diazotised and coupled.

It is a direct cotton dye, but does not go so readily on to the fibre as phenanthraquinone-2 : 7-bis-(2′)-azo-7′-amino-1′-hydroxynaphthalene-3′-sulphonic acid. It is not a good union dye.

2 : 7-*Diaminophenanthraquinonediphenylhydrazone*-pp′-*disulphonic Acid*, $C_{14}H_6(NH_2)_2[:N\cdot NH\cdot C_6H_4\cdot SO_3H]_2$.

A mixture of 1·2 grams of 2 : 7-diaminophenanthraquinone and 1·9 grams of phenylhydrazine-*p*-sulphonic acid was boiled with 20 c.c. of water. The diamino-quinone quickly disappeared and the whole mass became brown and pasty and entirely soluble in dilute sodium carbonate solution. After cooling, the insoluble matter was filtered off, and dissolved in dilute sodium hydroxide solution. The solution was filtered, carefully neutralised with sulphuric acid, and concentrated. After cooling, it was acidified with sulphuric acid and gave a brown precipitate consisting of crystalline aggregates. This was filtered off, washed, and dried in a vacuum (Found: N=15·0. $C_{26}H_{22}O_6N_6S_2$ requires N=14·5 per cent.).

It is an acid dye giving good warm brown shades on wool, but the dyeings are not particularly fast.

In conclusion, we wish to record our thanks to British Dyestuffs Corporation Limited, for permission to publish these results.

Dacca College,
East Bengal.

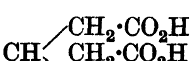
[*Received, May 2nd,* 1921.]

CXXXVI.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part II. Some Abnormal Condensations of Malonic and Cyanoacetic Esters with Halogenated Methanes.*

By CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL.

FOR the proper development of the general inquiry now being conducted in these laboratories into the conditions governing the formation from open-chain substances of carbon rings, and particularly of systems of associated rings, it has become necessary to undertake the preparation of a number of open-chain substances which either have never previously been prepared or have been obtained only in extremely small quantities. Amongst these are the higher polyacetic acids of methane, namely, methanetriacetic acid (I), the carboxytriacetic acid (II), the tetra-acetic acid (III), and the unsaturated triacetic acid (VI).

The necessity of devising methods for the preparation of such simply constituted substances is doubtless due to the fact that their synthesis is beset with experimental difficulties. The principal circumstances contributing to this result have been discussed in a recent paper (this vol., p. 341) by one of us, in which it is pointed out that the unsaturated acids IV, V, and VI, which have in their compositions one molecule of acetic acid less than the polyacetic acids I, II, and III respectively, and which therefore might be expected to yield these acids by the cyanoacetic ester method, are all substances of the "mobile" glutaconic type; in fact, in their stable forms they are not unsaturated. Such substances condense with ethyl cyanoacetate, usually only with difficulty and in any case in an abnormal manner, giving rise to 1 : 3-additive products as the "semi-aromatic" mode of formulation (VII, VIII, and IX)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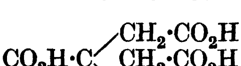
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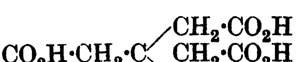
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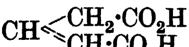
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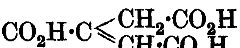
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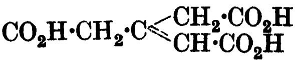
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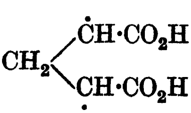
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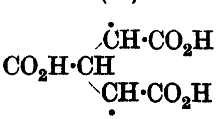
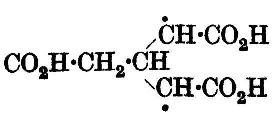
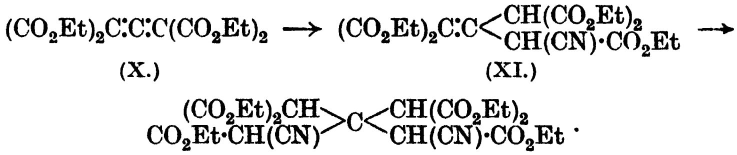

(VIII.)


(IX.)

requires. The difficulty of effecting the required condensation with the esters of the unsaturated acids IV, V, and VI, is therefore to be ascribed to the difficulty of obtaining these substances in a sufficiently stable condition owing to their tendency to pass into the "normal" isomerides VII, VIII, and IX.

In order, therefore, to obtain the required condensation product it is necessary to adopt some special means of ensuring that the glutaconic derivative shall react in its labile (unsaturated) form. One method of bringing about this result is to generate the appropriate labile glutaconic ester in the presence of ethyl sodiocyanoacetate and thus effect combination of the latter with the unsaturated ester in its "nascent" condition. This method has successfully been applied (*loc. cit.*) to the preparation of methanetriacetic acid and there seems every reason to suppose that the tetra-acetic acid (III) would be produced in a similar way if the unsaturated acid VI could be obtained and employed in its nascent condition.

A means of effecting this appeared to be provided in Zelinsky and Doroschewsky's allenetetracarboxylic ester (X), a substance which can easily be prepared in any desired quantity from carbon tetrachloride and malonic ester (*Ber.*, 1894, 27, 3374). This ester should react with ethyl cyanoacetate to form a derivative (XI) of the unsaturated acid VI, and, whatever changes of structure might occur during isolation, it must in the first place be produced in a form in which one of the two double bonds originally present in the allene derivative is preserved. If, therefore, the formation of this substance were to occur in the presence of ethyl sodiocyanoacetate, a further condensation with the nascent unsaturated ester should take place :



$$(CO_2Et)_2C{:}C{:}C(CO_2Et)_2 \longrightarrow (CO_2Et)_2C{:}C<\begin{matrix}CH(CO_2Et)_2\\ CH(CN)\cdot CO_2Et\end{matrix} \longrightarrow$$

(X.) (XI.)

$$\begin{matrix}(CO_2Et)_2CH\\ CO_2Et\cdot CH(CN)\end{matrix}>C<\begin{matrix}CH(CO_2Et)_2\\ CH(CN)\cdot CO_2Et\end{matrix}\cdot$$

(XII.)

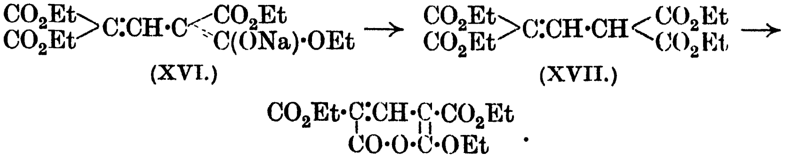
The ultimate product (XII) should yield methanetetra-acetic acid on hydrolysis.

There seemed every reason for anticipating that these reactions would proceed with ease, for in the first place Zelinsky and Doroschewsky had shown that allenetetracarboxylic ester is a substance having strong additive properties, and in the second place the intermediate glutaconic derivative (XI) contains a number of α-substituents, a condition which always confers stability on the unsaturated modification. We were therefore considerably surprised to find in the product of the condensation no trace of the esters XI or XII or of any product which might have been derived from them. Ultimately, the reason for the discrepancy was discovered in the fact that Zelinsky and Doroschewsky's "allenetetracarboxylic ester" was not an allene derivative, and, moreover, was not even a substance having the same empirical composition.

The initial product which Zelinsky and Doroschewsky obtained by the condensation of carbon tetrachloride and ethyl sodiomalonate was a yellow sodium compound, to which they gave the formula XIII. On treating this with dilute acids, the sodium was displaced by hydrogen, and there was produced an oily unsaturated ester (XIV), which on distillation eliminated alcohol and yielded the crystalline ester (X):

$$\underset{\text{(XIII.)}}{(CO_2Et)_2C{:}CNa{\cdot}C(OEt)(CO_2Et)_2} \longrightarrow \underset{\text{(XIV.)}}{(CO_2Et)_2C{:}CH{\cdot}C(OEt)(CO_2Et)_2} \longrightarrow \text{(X.)}$$

On repeating the experiment under the exact conditions used by Zelinsky and Doroschewsky, we found no difficulty in confirming their results in every particular excepting as regards the compositions and chemical characters of the substances isolated. Contrary to the conclusion of these investigators, however, the yellow sodium compound proved to be, not the ethoxy-derivative XIII, but the well-known substance first obtained by Conrad and Guthzeit by the condensation of chloroform with ethyl sodiomalonate (*Ber.*, 1882, **15**, 284); this substance (XVI) on acidification gave the ester to which Zelinsky and Doroschewsky ascribed the formula XIV, but which in reality is ethyl dicarboxyglutaconate (XVII); this, on distillation, passed into the solid ester which they regarded as an allene derivative, but which actually was the well-known ethoxylactone, XVIII:



$$\begin{matrix}CO_2Et\\CO_2Et\end{matrix}\!>\!C{:}CH{\cdot}C\!<\!\begin{matrix}CO_2Et\\C(ONa){\cdot}OEt\end{matrix} \rightarrow \begin{matrix}CO_2Et\\CO_2Et\end{matrix}\!>\!C{:}CH{\cdot}CH\!<\!\begin{matrix}CO_2Et\\CO_2Et\end{matrix} \rightarrow$$

(XVI.) (XVII.)

$$\begin{array}{l}CO_2Et{\cdot}C{:}CH{\cdot}C{\cdot}CO_2Et\\ \qquad\;\; CO{\cdot}O{\cdot}C{\cdot}OEt\end{array}$$

(XVIII.)

All these substances yielded glutaconic acid on hydrolysis and were further identified by analysis and by direct comparison with authentic specimens.

It must not be supposed that the production of these substances is due to the presence of chloroform as an impurity in the carbon tetrachloride used. Even that used in our earliest experiments was quite pure, distilling completely at an almost constant temperature. Moreover, the sample contained no trace of hydrogen and gave correct figures on complete analysis. Further, it did not reduce Fehling's solution, whilst carbon tetrachloride containing 5 per cent. of chloroform readily attacked this reagent. Now, if the production of the yellow sodium compound is to be explained by assuming the presence of chloroform in the carbon tetrachloride, it would be necessary to suppose that at least 30 per cent. of chloroform was contained in the sample with which these tests and analyses were carried out. That clearly is impossible. In order to settle the matter beyond question, the effect was tried of using carbon tetrachloride which had been recovered from a previous condensation. If the production of the yellow sodium compound is due to the interaction of chloroform and ethyl sodiomalonate, the recovered carbon tetrachloride should be almost free from the reactive impurity and should yield little or no yellow sodium compound on condensing again in the same way. Actually, the quantity of the sodium compound produced was undiminished. The same yield was obtained from carbon tetrachloride which had been treated with hot 6·5*N*-methyl-alcoholic potassium hydroxide, and even from carbon tetrachloride which had been subjected to prolonged boiling with Fehling's solution. There can be no question, therefore, but that the carbon tetrachloride itself is responsible for the formation of the yellow sodium compound XVI, and that it supplies the central carbon atom of that substance.

In order to obtain, if possible, some information as to the mechanism of this remarkable change, the interaction of carbon tetrachloride and ethyl sodiocyanoacetate was next investigated. If carbon tetrachloride condensed normally with this sodio-ester, the product should be dicyanoallenedicarboxylic ester (XIX); if, on the other hand, the carbon tetrachloride behaved as though it were chloroform, the product should be αγ-dicyanoglutaconic ester (XX), an easily isolated crystalline substance, which has been well characterised by Ruhemann and Browning (T., 1898, **73**, 282) as well as by subsequent workers. Actually, the product of the

$$CO_2Et\cdot(CN)C{:}C{:}C(CN)\cdot CO_2Et \qquad CO_2Et(CN)CH\cdot CH{:}C(CN)\cdot CO_2Et$$

(XIX.) (XX.)

condensation was dicyanoglutaconic ester, proving that here again carbon tetrachloride had reacted as though it were chloroform.

In the course of this reaction a large quantity of cyanoacetamide (XXII) was invariably produced. This at first sight appears extraordinary, for in no stage of the reaction which results in the formation of dicyanoglutaconic ester can it be supposed that two $\cdot C\vdots N$ or $\cdot \ddot{C}\cdot N{:}$ groups become attached to the same carbon atom, The difficulty was, however, to a large extent removed when it was discovered that, along with the cyanoacetamide, there was present another crystalline by-product, namely, ethyl α-cyano-β-iminoglutarate (XXI), a substance originally prepared by Best and Thorpe (T., 1909, **95**, 1518) by condensing ethyl cyanoacetate with its sodium derivative. Obviously, therefore, ethyl cyanoacetate must have been liberated during the condensation (probably by the action of the distinctly acidic dicyanoglutaconic ester), and must then have combined with some of the unchanged sodio-derivative, forming ethyl α-sodio-α-cyano-β-iminoglutarate, from which the free cyanoimino-ester would doubtless be liberated by a similar mechanism :

$$\mathrm{CH_2(CN)\cdot CO_2Et + CH(CN){:}C(ONa)\cdot OEt} \longrightarrow$$
$$\mathrm{CO_2Et\cdot CH_2\cdot C({:}NH)\cdot C(CN){:}C(ONa)\cdot OEt} \longrightarrow$$
$$\mathrm{CO_2Et\cdot CH_2\cdot C({:}NH)\cdot CH(CN)\cdot CO_2Et.}$$

(XXI.)

The imino-derivative, in its aminoglutaconic modification, must then have undergone fission at the double bond, producing ethyl cyanomalonamate, which, in the presence of hot sodium ethoxide, would break down into cyanoacetamide and ethyl carbonate :

$$\mathrm{CO_2Et\cdot CH\overset{\cdot}{\underset{\cdot}{=}}C(NH_2)\cdot CH(CN)\cdot CO_2Et} \longrightarrow \mathrm{CH(CN)(CO\cdot NH_2)\cdot CO_2Et} \longrightarrow$$
$$\mathrm{CH_2(CN)\cdot CO\cdot NH_2 + CO(OEt)_2.}$$

(XXII.)

In this reaction there must also have been formed a product derived from the residue $\mathrm{CO_2Et\cdot CH{:}}$ to the left of the dotted line. The nature of this product is unknown, but at least it is certain that it was not ethyl butyrate, the substance to be expected had the fission reaction been of the nature of an alcoholysis. Since, however, the production of dicyanoglutaconic ester requires the oxidation of *some* organic material in order to provide the necessary two atoms of hydrogen, we consider it probable that the $\mathrm{CO_2Et\cdot CH{:}}$ residue gave rise to an oxidation product such as glyoxylic ester or some polymeride of that substance, although no experimental evidence could be discovered to support this view.

The source of the two hydrogen atoms necessary for the production of Conrad and Guthzeit's sodium compound from carbon tetrachloride and malonic ester is even more obscure, but there is indirect evidence pointing to the oxidation of alcohol as the probable source. For, whilst carbon tetrachloride, by treatment with benzene and aluminium chloride, yields the normal product, triphenylchloromethane (Gomberg, *Ber.*, 1900, **33**, 3144), on heating with alcoholic potassium hydroxide gives rise to potassium formate (Nef, *Annalen*, 1899, **308**, 330) and with sodium ethoxide to orthoformic ester, substances the production of which undoubtedly involves the oxidation of alcohol. Deeply coloured resinous by-products are always obtained in these reactions.

The apparent impossibility of obtaining a normal condensation product from carbon tetrachloride by the action of ethyl sodiomalonate or ethyl sodiocyanoacetate is of some significance in view of the fact that trichloroacetic ester yields no condensation product with either of these substances under the usual experimental conditions (Professor J. F. Thorpe, private communication); for it would seem to follow that no halogenated derivative of methane can react normally with such sodio-esters unless at least one hydrogen atom is attached to the carbon. If this is so, it is doubtless no more than a phase of the general law that the production of a condition of unsaturation (which in these instances would involve bivalent carbon) is necessary to all organic reactions.

In order to test the matter as completely as possible, the behaviour towards ethyl sodiocyanoacetate and ethyl sodiomalonate of two other halogenated methanes was examined. The substances chosen were carbon tetrabromide and chloropicrin and the results obtained were in complete harmony with the general hypothesis; for in neither case could a trace of the normal condensation product be isolated. The main products were ethyl dicyanosuccinate or ethyl ethanetetracarboxylate according to the sodio-ester employed.

EXPERIMENTAL.

(A) *Purification of Carbon Tetrachloride.*

The carbon tetrachloride employed in the following experiments was prepared for use by four methods.

(*a*) *Distillation.*—The commercial material was found to boil almost constantly at 77° and a middle fraction having a boiling point which appeared to be absolutely constant was therefore collected for use. Its purity was controlled by analysis (Found: C=7·6; Cl=91·8. Calc., C=7·8; Cl=92·2 per cent.), and by the absence of any reaction with Fehling's solution at 60°. This clearly proves that no considerable quantity of chloroform can be present, since the addition of 5 per cent. of chloroform to the carbon tetrachloride caused rapid reduction of the Fehling's solution to occur under the same experimental conditions.

(*b*) *Digestion with Fehling's Solution.*—In order to remove any trace of chloroform present, the distilled carbon tetrachloride was digested with Fehling's solution for several hours at 60—70°. The flask was vigorously shaken from time to time, and, finally, the lower layer was removed, dried, and refractionated.

(*c*) *Treatment with Alcoholic Potassium Hydroxide.*—The distilled carbon tetrachloride was treated with about 2 molecules of potassium hydroxide in 6·5*N*-methyl-alcoholic solution. When the addition was complete, the mixture was heated on a steam-bath for thirty minutes and then kept at room temperature overnight. The unchanged carbon tetrachloride was then recovered by adding water and collecting in ether and was finally purified by fractional distillation.

(*d*) *Treatment with Ethyl Sodiomalonate.*—Distilled carbon tetrachloride was condensed with ethyl sodiomalonate in alcoholic solution under the conditions given below for the preparation of ethyl sodiodicarboxyglutaconate from carbon tetrachloride. The product was worked up in the usual way and, after the yellow sodium compound had been removed, the oily product was extracted with ether and divided into neutral and acid fractions by means of sodium carbonate. The unchanged carbon tetrachloride was then recovered from the neutral fraction by distillation.

(B) *Action of Sodium Ethoxide on Carbon Tetrachloride.*

Carbon tetrachloride was boiled for forty-eight hours with an absolute alcoholic solution containing four molecular proportions of sodium ethoxide. The product, although still having a faintly alkaline reaction, was concentrated by evaporation and poured into water. The oil was extracted with ether and the extract washed several times with water, dried, and evaporated. The residue, on distillation, yielded three main fractions: (*a*) a small fraction, b. p. 70—90°, (*b*) a large fraction, b. p. 135—150°, (*c*) a small fraction, b. p. 150—168°. Fraction (*a*) consisted essentially of unchanged carbon tetrachloride, fraction (*b*) of ethyl orthoformate, whilst fraction (*c*) may have contained ethyl orthocarbonate, although this substance was not isolated owing to the smallness of the quantity.

Ethyl Orthoformate, $CH(OC_2H_5)_3$.

This ester was obtained (b. p. 143—145°) by distilling fraction (*b*) until the distillate was free from chlorine (Found: C=57·1; H=10·8. Calc., C=56·8; H=10·8 per cent.).

(C) *Condensation of Carbon Tetrachloride with Ethyl Sodiomalonate.*

This condensation was carried out by the method given by Zelinsky and Doroschewsky (*loc. cit.*) for the preparation of the additive product of ethyl allenetetracarboxylate and sodium ethoxide. The dark red product was filtered and the filtrate concentrated by distillation until the alcohol had been almost entirely removed. Water and ice were then added and the crystalline solid thus precipitated was collected.

Ethyl Sodiodicarboxyglutaconate (XVI).

The solid product was first purified by washing successively with water, cold alcohol, and ether, and was finally crystallised from alcohol. It was thus obtained as bright yellow needles and was identified as ethyl sodiodicarboxyglutaconate by analysis (Found: Na=6·4. Calc., Na=6·5 per cent. A number of estimations were made, but we were unable to obtain a figure approaching that recorded by Zelinsky and Doroschewsky for this substance), by direct comparison with a specimen prepared from chloroform and ethyl sodiomalonate, by conversion into the two derivatives mentioned below, and by hydrolysis to glutaconic acid.

Ethyl Dicarboxyglutaconate (XVII).

This ester was prepared by shaking the sodium compound with dilute hydrochloric acid and ether until the yellow colour had vanished and then drying and evaporating the ethereal solution (Found: C=54·2; H=6·7. Calc., C=54·55; H=6·7 per cent.). On hydrolysis it yielded glutaconic acid.

Ethyl 6-*Ethoxy*-2-*pyrone*-3 : 5-*dicarboxylate* (XVIII).

The liquid ester, on distillation under diminished pressure, quickly eliminated ethyl alcohol and yielded the pyrone, which passed over at 200°/10 mm. and separated from dry ether in needles melting at 94°. It was identified by analysis * (Found: C=54·7; H=5·8. Calc., C=54·9; H=5·6 per cent.), by direct comparison and by a mixed melting point determination with an authentic specimen, and, finally, by hydrolysis to glutaconic acid.

(D) *Condensation of Carbon Tetrachloride with Ethyl Sodiocyanoacetate.*

An alcoholic solution containing four molecules of ethyl sodiocyanoacetate and one of carbon tetrachloride was heated at 100°

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* The percentages calculated for ethyl allenetetracarboxylate (C=54·9; H=6·1) approximate rather closely to those for the true formula, a circumstance which probably contributed to Zelinsky and Doroschewsky's misapprehension.

for four hours. The mixture was then cooled and the solid material which had separated was collected with the aid of the pump. The filtrate was evaporated under reduced pressure, poured into water, and extracted with ether, the extracted material being separated by sodium carbonate in the usual manner into neutral and acid fractions.

Ethyl αγ-Dicyanoglutaconate (XX).

On drying and evaporating the acid extract there was obtained a solid residue which, when crystallised from alcohol, melted at 183—184°. It was identified as ethyl αγ-dicyanoglutaconate by direct comparison and by a mixed melting point determination with a specimen prepared from ethyl cyanoacetate and chloroform (Found: C=53·9; H=6·4. Calc., C=55·9; H=5·1 per cent.*).

Ethyl α-Cyano-β-iminoglutarate (XXI).

The neutral extract, on evaporation, yielded a crystalline residue which separated from ethyl bromide in needles melting at 53° (compare Best and Thorpe, *loc. cit.*) (Found: C=52·8; H=6·45. Calc., C=53·1; H=6·2 per cent.).

Cyanoacetamide (XXII).

The solid on the filter was washed with hot alcohol and the residue obtained on evaporation of the washings crystallised from alcohol. The material thus obtained melted at 120° and was identified as cyanoacetamide by analysis (Found: C=42·6; H=4·9. Calc., C=42·85; H=4·75 per cent.), and by direct comparison and a mixed melting-point determination with a known specimen.

(E) *Condensation of Carbon Tetrabromide with Ethyl Sodiomalonate and with Ethyl Sodiocyanoacetate.*

These condensations were conducted similarly to the condensations with carbon tetrachloride and the substances formed were isolated in the same way. The principal product proved to be ethyl ethanetetracarboxylate or ethyl αα′-dicyanosuccinate, according to the sodio-ester employed. On hydrolysis with dilute sulphuric acid, succinic acid was obtained and in the case of the ethanetetracarboxylic ester the material was also identified by direct comparison and by a mixed melting-point determination with a known specimen (Found: C=52·9; H=7·0. Calc., C=52·8; H=6·9 per cent.).

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* The poor results obtained on combustion are undoubtedly due to the difficulty of obtaining anhydrous specimens (compare Ruhemann and Browning, *loc. cit.*, and Errera, *Gazzetta*, 1879, **27**, [ii], 393).

(F) *Condensation of Chloropicrin with Ethyl Sodiomalonate and with Ethyl Sodiocyanoacetate.*

With the exception that owing to the large amount of heat which is developed it is necessary to add the chloropicrin to the sodio-esters very slowly, these condensations were carried out like the condensations with carbon tetrabromide and gave the same results.

We desire to record our thanks to Professor J. F. Thorpe for his valuable suggestions and criticism and to the Chemical Society for a grant which has defrayed a large part of the cost of this investigation.

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SOUTH KENSINGTON, S.W.7. [*Received, May 25th,* 1921.]

CXXXVII.—*The Formation and Properties of Dithioketones* ($R_2C{:}S{:}S$) *and Dithio-ethers* ($R_2S{:}S$). *Part II.*

By KUVERJI GOSAI NAIK.

THE experiments described in this paper afford clear evidence that the interaction of sulphur monochloride with compounds containing the methylene radicle depends on the nature of the groups attached to the two remaining valencies of the carbon atom. Thus, if these valencies carry neutral groups such as $CO{\cdot}NH_2$, for example, in malonamide, $CH_2(CO{\cdot}NH_2)_2$, no reaction occurs. If, however, one of these carboxyamido-groups is replaced by the carbethoxy-group, as in ethyl malonamate, $CH_2(CO_2Et){\cdot}CO{\cdot}NH_2$, or if the neutral character of either or both of the carboxyamido-groups is disturbed by the substitution of a phenyl, tolyl, or similar group at the nitrogen atom, as in the compounds $CH_2(CO{\cdot}NH_2){\cdot}CO{\cdot}NHPh$, $CH_2(CO{\cdot}NH{\cdot}C_{10}H_7)_2$, $CH_2(CO{\cdot}NH{\cdot}C_7H_7)_2$, interaction with sulphur monochloride readily occurs with the formation of dithioketones of the type $S{:}S{:}C(CO{\cdot}NH_2){\cdot}CO{\cdot}NHPh$.

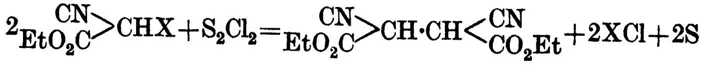
Moreover, although no definite measurements have as yet been made, it is evident that the speed of the reaction depends on the electronegative character of the attached groups. For example, sulphur monochloride reacts more vigorously with malondiphenylamide, $CH_2(CO{\cdot}NHPh)_2$, than with malonomonotolylamide, $CH_2(CO{\cdot}NH_2){\cdot}CO{\cdot}NH{\cdot}C_7H_7$, and the reaction with ethyl malonotolylamate, $CH_2(CO_2Et){\cdot}CO{\cdot}NH{\cdot}C_7H_7$, is still more vigorous than with either of the former compounds. In fact, reactions of the last-named type take place at the ordinary temperature with copious evolution of hydrogen chloride.

Wolff and Ott (*Ber.*, 1903, **36**, 3721) have studied the interaction of methyl and ethyl malonates with sulphur monochloride in the presence of anhydrous aluminium chloride and obtained different compounds with the two esters. Since it is well known that sulphur monochloride reacts in different ways under different conditions (Böeseken, *Rec. trav. chim.*, 1905, **24**, 209; Cohen and Skirrow, T., 1899, **75**, 887; P., 1899, **15**, 183; Claus and Krall, *Ber.*, 1871, **4**, 99; Edeleano, *Bull. Soc. chim.*, 1891, [iii], **5**, 173; Roorda Smit, *Ber.*, 1875, **8**, 1445), it was decided to study its reaction with (1) malonic and cyanoacetic esters and (2) their sodium compounds. It is remarkable that the products of these condensations are, in the case of the malonic ester, ethyl ethylenetetracarboxylate, and in the case of the cyanoacetic ester, ethyl dicyanosuccinate, whilst for the sodium compounds they are ethyl ethanetetracarboxylate in the case of the malonic ester, and ethyl dicyanosuccinate in the case of the cyanoacetic ester. A separation of sulphur occurs in every case :

$$2(EtO_2C)_2CHNa+S_2Cl_2=(EtO_2C)_2CH{\cdot}CH(CO_2Et)_2+2NaCl+2S$$

$$2(EtO_2C)_2CH_2+2S_2Cl_2=(EtO_2C)_2C{:}C(CO_2Et)_2+4HCl+4S$$

and



$$2\left.\begin{matrix}CN\\EtO_2C\end{matrix}\right>CHX+S_2Cl_2=\left.\begin{matrix}CN\\EtO_2C\end{matrix}\right>CH{\cdot}CH\left<\begin{matrix}CN\\CO_2Et\end{matrix}\right.+2XCl+2S$$

where X=H or Na.

It has been mentioned in Part I of this series (this vol., p. 382) that dithiomesoxanilide, when nitrated with fuming nitric acid, yields a tetranitro-derivative :

$$S{:}S{:}C(CO{\cdot}NHPh)_2 \longrightarrow S{:}S{:}C(CO{\cdot}NH{\cdot}C_6H_3[NO_2]_2)_2.$$

The reaction has now been extended to other dithioketones, for example, to dithiomesoxo-α-naphthylamide, which in the first place gives a tetranitro-derivative :

$$S{:}S{:}C(CO{\cdot}NH{\cdot}C_{10}H_7)_2 \longrightarrow S{:}S{:}C(CO{\cdot}NH{\cdot}C_{10}H_5[NO_2]_2)_2.$$

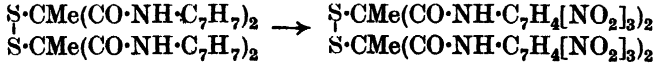
When, however, nitration is carried further, the dithio-grouping is broken down and a sulphoxide results, two more nitro-group entering the naphthalene nuclei at the same time:

$$S{:}S{:}C(CO{\cdot}NH{\cdot}C_{10}H_5[NO_2]_2)_2 \longrightarrow O{:}S{:}C(CO{\cdot}NH{\cdot}C_{10}H_4[NO_2]_3)_2.$$

(I.)

Dithiomesoxo-β-naphthylamide and *o*- and *p*-toluidides behave in the same way.

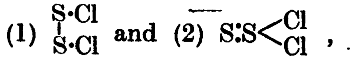
An example of the nitration of a disulphide is furnished by methylmalono-*p*-toluidide disulphide, which, on very careful nitration, yields a dodecanitro-compound:



$$\begin{matrix} S{\cdot}CMe(CO{\cdot}NH{\cdot}C_7H_7)_2 \\ | \\ S{\cdot}CMe(CO{\cdot}NH{\cdot}C_7H_7)_2 \end{matrix} \longrightarrow \begin{matrix} S{\cdot}CMe(CO{\cdot}NH{\cdot}C_7H_4[NO_2]_3)_2 \\ | \\ S{\cdot}CMe(CO{\cdot}NH{\cdot}C_7H_4[NO_2]_3)_2 \end{matrix}.$$

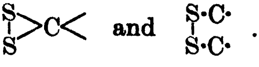
(II.)

Clearly, therefore, it is possible to nitrate these compounds without destroying the dithio-grouping, which behaves as a remarkably stable residue. This is obviously a powerful argument in support of the view previously suggested that the dithio-grouping in these compounds is structurally different from that present in ββ'-dichlorodiethyl disulphide and similar compounds and that sulphur monochloride is capable of reacting in two forms,



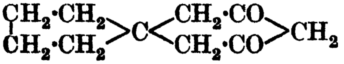
$$(1)\ \begin{matrix} S{\cdot}Cl \\ | \\ S{\cdot}Cl \end{matrix} \text{ and } (2)\ S{:}S{<}\begin{matrix} Cl \\ Cl \end{matrix},$$

the first of which gives rise to very stable dithio-compounds (compare Part I of this series) containing the groups



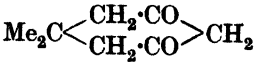
$$\begin{matrix} S \\ | \\ S \end{matrix}{>}C{<} \text{ and } \begin{matrix} S{\cdot}C{\cdot} \\ | \\ S{\cdot}C{\cdot} \end{matrix}.$$

Experiments have been carried out with the object of testing the reactivity of sulphur monochloride towards compounds containing the group $-CO{\cdot}CH_2{\cdot}CO-$, when the latter forms a part of a closed ring, and as a large amount of work is being done in this laboratory on the formation and stability of *spiro*-compounds, it was decided to employ typical *spiro*-compounds containing a *cyclo*hexane ring. Three such compounds (III), (IV), and (V) (compare Norris and Thorpe, this vol., p. 1190) were selected:



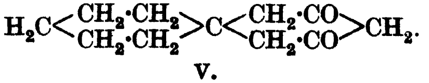
$$\begin{matrix} CH_2{\cdot}CH_2 \\ | \\ CH_2{\cdot}CH_2 \end{matrix}{>}C{<}\begin{matrix} CH_2{\cdot}CO \\ CH_2{\cdot}CO \end{matrix}{>}CH_2$$

(III.)



$$Me_2C{<}\begin{matrix} CH_2{\cdot}CO \\ CH_2{\cdot}CO \end{matrix}{>}CH_2$$

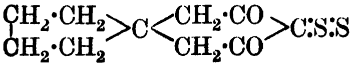
(IV.)



$$H_2C{<}\begin{matrix} CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH_2 \end{matrix}{>}C{<}\begin{matrix} CH_2{\cdot}CO \\ CH_2{\cdot}CO \end{matrix}{>}CH_2.$$

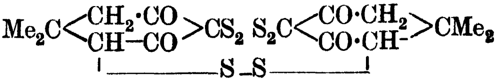
V.

The course pursued in these reactions affords a remarkable example of the difference in the behaviour of similarly constituted substances containing the $-\text{CO}\cdot\text{CH}_2\cdot\text{CO}-$ group towards sulphur monochloride. For, whilst in the compound (III) only one methylene group, namely, that situated between the carbonyl groups, is attacked, with the formation of the dithioketone (VI), in the compound (IV) the reaction proceeds further and involves one of the remaining methylene groups of the dihydroresorcinol ring, the substance (VII) being formed, and in the case of the *spiro*-compound (V), it proceeds yet further, all three of the methylene groups being attacked. The product in this case is the compound (VIII).



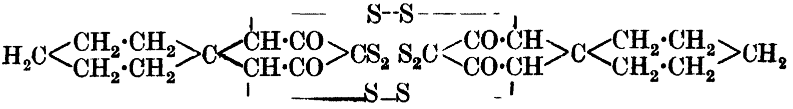
$$\begin{matrix}\text{CH}_2\cdot\text{CH}_2\\ \text{CH}_2\cdot\text{CH}_2\end{matrix}\!>\!\text{C}\!<\!\begin{matrix}\text{CH}_2\cdot\text{CO}\\ \text{CH}_2\cdot\text{CO}\end{matrix}\!>\!\text{C:S:S}$$

(VI.)



$$\text{Me}_2\text{C}\!<\!\begin{matrix}\text{CH}_2\cdot\text{CO}\\ \text{CH}-\text{CO}\end{matrix}\!>\!\text{CS}_2\ \text{S}_2\text{C}\!<\!\begin{matrix}\text{CO}\cdot\text{CH}_2\\ \text{CO}\cdot\text{CH}-\end{matrix}\!>\!\text{CMe}_2$$
$$\text{S}-\text{S}$$

(VII.)

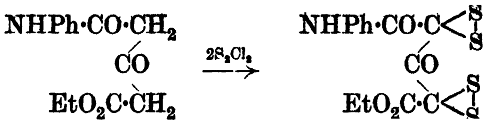


$$\text{S}-\text{S}$$
$$\text{H}_2\text{C}\!<\!\begin{matrix}\text{CH}_2\cdot\text{CH}_2\\ \text{CH}_2\cdot\text{CH}_2\end{matrix}\!>\!\text{C}\!<\!\begin{matrix}\text{CH}\cdot\text{CO}\\ \text{CH}\cdot\text{CO}\end{matrix}\!>\!\text{CS}_2\ \text{S}_2\text{C}\!<\!\begin{matrix}\text{CO}\cdot\text{CH}\\ \text{CO}\cdot\text{CH}\end{matrix}\!>\!\text{C}\!<\!\begin{matrix}\text{CH}_2\cdot\text{CH}_2\\ \text{CH}_2\cdot\text{CH}_2\end{matrix}\!>\!\text{CH}_2$$
$$\text{S}-\text{S}$$

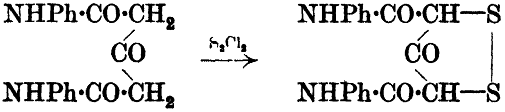
(VIII.)

In order to obtain further knowledge of the influence on the reaction of sulphur monochloride with methylene groups of neighbouring electronegative residues, experiments with substituted amides containing the group $-\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}-$ were made. The compounds employed were (1) the dianilide, (2) the di-*o*-toluidide, (3) the di-*p*-toluidide, of acetonedicarboxylic acid, and (4) ethyl γ-phenylcarbamylacetoacetate.

Of these compounds, only (1) and (4) have been described (Besthorn and Garben, *Ber.*, 1900, **33**, 3443), whereas (2) and (3) do not appear to have been prepared. When these four compounds were treated with sulphur monochloride in dry benzene, reaction took place readily, but it was most vigorous in the case of compound (4), the product containing four atoms of sulphur. In cases (1), (2), and (3), although more than two molecules of sulphur monochloride were taken for every molecule of the substituted amide to give ample opportunity for the substitution of dithio-groups for all the hydrogen atoms in the two reactive methylene groups, reaction did not proceed to this extent and the product contained only two atoms of sulphur, one hydrogen atom of each methylene group having been substituted.



(IX.)



(X.)

This is in accord with what follows from the hypothesis herein suggested, that the reactivity of the two hydrogen atoms of the methylene group is dependent on the total negativity of the two carbonyl groups with their attached radicles. It will be seen in the case of the foregoing substituted amides that the negative effect of the central carbonyl group is divided between the two adjacent methylene groups, so that the total negative effect on each methylene group is smaller than that on a single methylene group when linked as $-CO·CH_2·CO-$, as in the case of the compounds described in Part I. Hence it is to be expected that the two methylene groups in compounds (1), (2), and (3) will be less reactive than the methylene group in compounds such as malonanilide. However, as soon as the total negativity of the compound is increased by replacing one of the CO·NHR groups by a carbethoxy-group, the reactivity is correspondingly increased, and a dithio-compound is produced, analogous to those described above.

The investigation of the exact conditions under which the stability of the dithio-group can be controlled will be the subject of future work.

EXPERIMENTAL.

*Dithiomesoxo-*p*-toluidide.*

Malono-*p*-toluidide was prepared by the method of Whiteley (T., 1903, **83**, 24) with the modification introduced by Reissert and Moré (*Ber.*, 1906, **39**, 3300). The best temperature for the condensation is, in this instance, 140°, rising to 160°. The amide (10 grams), sulphur monochloride (5 grams) and benzene (100 grams) were heated together for three hours, and the solid condensation product was then washed with dry benzene and purified by precipitation from its solution in acetone by means of water until it melted at 215—216° (Found: S=18·26. $C_{17}H_{16}O_2N_2S_2$ requires S=18·60 per cent.).

The *tetranitro*-derivative was prepared by dissolving the thio-compound in sufficient nitric acid (D 1·5) and warming. The nitration product which separated on cooling was collected, washed with concentrated nitric acid and with water, and dried, when it was obtained as white crystals which melted and decomposed at 255° and assumed a yellow colour on keeping (Found : N=15·81; S=11·82. $C_{17}H_{12}O_{10}N_6S_2$ requires N=16·03; S=12·21 per cent.).

Dithiomesoxo-o-*toluidide.*

Malono-*o*-toluidide was prepared and condensed with sulphur monochloride similarly to the *para*-compound. The product obtained by evaporating the solvent (benzene) was crystallised from a mixture of benzene and light petroleum. It separated in fibrous needles melting at 189—190° (Found: S=18·89. $C_{17}H_{16}O_2N_2S_2$ requires S=18·60 per cent.).

The *tetranitro*-derivative was prepared in the same way as the *p*-isomeride and obtained as a yellowish-white powder when the solution in nitric acid was allowed to cool slowly. It melted and decomposed at 165° (Found : N=16·15; S=12·32. $C_{17}H_{12}O_{10}N_6S_2$ requires N=16·03; S=12·21 per cent.).

Dithiomesoxo-α-*naphthylamide.*

Malonodi-α-naphthylamide (6·5 grams), prepared like the toluidide except that the final temperature was 170°, sulphur monochloride (2·5 grams) and benzene (50 c.c.) were heated together and the product was purified by crystallisation from benzene. It formed pale red needles which sintered at 160° and melted with decomposition at 210° (Found : S=15·70. $C_{23}H_{16}O_2N_2S_2$ requires S=15·38 per cent.).

Tetranitro-derivative.—The dithio-amide (5 grams) was treated gradually with 40 c.c. of nitric acid (D 1·5). After the first violence of the reaction had abated, the mixture was warmed to complete it and then allowed to cool, when the tetranitro-compound separated as an orange-red powder. After being washed with concentrated nitric acid and with water, it melted at 190° with decomposition (Found : N=14·43; S=10·40. $C_{23}H_{12}O_{10}N_6S_2$ requires N=14·09; S=10·75 per cent.).

Hexanitro-sulphoxide (Formula I).—This was recovered from the nitric acid washings by dilution with water as a yellow, crystalline substance which decomposed at 135° (Found : N=16·81; S=4·57. $C_{23}H_{10}O_{15}N_8S$ requires N=16·71; S=4·77 per cent.).

Dithiomesoxo-β-*naphthylamide.*

Malonodi-β-naphthylamide was prepared similarly to the α-compound and condensed in the same way. The product was purified by repeated precipitation by water from its solution in acetone until it melted at 204° with decomposition (Found: S=15·56. $C_{23}H_{16}O_2N_2S_2$ requires S=15·38 per cent.).

The *tetranitro*-derivative, when prepared and purified as in the case of the α-naphthylamine derivative, was obtained as a pale yellow powder decomposing at 195° (Found: N=14·04; S=10·54. $C_{23}H_{12}O_{10}N_6S_2$ requires N=14·10; S=10·73 per cent.).

Dithiomesoxomono-p-*toluidide.*

Malonomono-*p*-toluidide, prepared by Whiteley's method (*loc. cit.* Compare also Backes, West, and Whiteley, this vol., p. 372), the temperature of the condensation with *p*-toluidine being 120—125°, was condensed (7 grams) with sulphur monochloride (5 grams) in benzene (50 grams) in the usual manner. The product separated from alcohol, on addition of water, in short needles which melted to an oil clarifying at 150° and decomposing at 165° (Found: S=24·78. $C_{10}H_{10}O_2N_2S_2$ requires S=25·20 per cent.).

Dithiomesoxomonophenylamide.

Malonomonophenylamide, prepared like the toluidide, was condensed with sulphur monochloride in a similar way. The product separated from acetone, in which it was sparingly soluble, in short needles, melting and decomposing at 202° (Found: S=26·9. $C_9H_8O_2N_2S_2$ requires S=26·66 per cent.).

Ethyl Dithiomesoxo-p-*tolylamate.*

Ethyl malono-*p*-tolylamate, prepared by Whiteley's method (*ibid.*, pp. 36, 40) at 120—125°, was condensed (8 grams) with sulphur monochloride (5 grams) in benzene (50 c.c.) in the usual way. The reaction began in the cold, with copious evolution of hydrogen chloride. The liquid was cooled and filtered and the solvent was allowed to evaporate. The semi-solid mass was redissolved in benzene, and solidified when the solution was cooled with ice. It sintered at 74° and melted at 90° (Found: S=22·44. $C_{12}H_{13}O_3NS_2$ requires S=22·61 per cent.).

Ethyl Dithiomesoxo-o-*tolylamate.*

This substance was prepared like the *para*-compound and was purified by repeated spontaneous evaporation of its solution in benzene and finally in ether. It melted at 62° (Found: S=22·48. $C_{12}H_{13}O_3NS_2$ requires S=22·61 per cent.).

Methylmalono-p-*toluidide Disulphide* (Formula II).

Methylmalono-p-*toluidide* was prepared from ethyl methylmalonate (9 grams) and *p*-toluidine (10 grams) in the same way as the lower homologue previously mentioned, except that in this case the temperature was 160° rising to 180°. It separated in a very pure condition and after crystallisation from acetic acid melted at 220° (Found: N=9·79. $C_{18}H_{20}O_2N_2$ requires N=9·46 per cent.).

The above amide (8 grams) and sulphur monochloride (2 grams) were allowed to react in benzene (100 c.c.) in the usual manner. The solution was cooled and filtered and the solvent was allowed to evaporate. The residue was again dissolved in benzene and the product was crystallised from a mixture of benzene and light petroleum and then melted at 224—225° (Found: S=10·19. $C_{36}H_{38}O_4N_4S_2$ requires S=9·78 per cent.).

The *dodecanitro*-derivative was obtained by the regulated action of fuming nitric acid and precipitated by the addition of water. At no time should the liquid be allowed to boil. After being filtered and washed with nitric acid and with water, it was obtained as a pale yellow powder decomposing at 140° (Found: N=18·50; S=5·61. $C_{36}H_{26}O_{28}N_{16}S_2$ requires N=18·76; S=5·36 per cent.).

Methylmalono-o-*toluidide Disulphide.*

Methylmalono-o-*toluidide* was prepared and purified like the *para*-compound. It melted at 161° (Found: N=9·52. $C_{18}H_{20}O_2N_2$ requires N=9·46 per cent.).

The amide was condensed with sulphur monochloride as in the case of the *para*-compound; the product crystallised from alcohol in mealy crystals which melted at 174° (Found: S=10·09. $C_{36}H_{38}O_4N_4S_2$ requires S=9·78 per cent.).

Methylmalonomono-o-*toluidide Disulphide*,
$S_2[CMe(CO{\cdot}NH_2){\cdot}CO{\cdot}NH{\cdot}C_7H_7]_2$.

Methylmalonomono-o-*toluidide* was prepared from ethyl methylmalonate (22 grams) and *o*-toluidine (9 grams) in a similar manner as malonomono-*p*-toluidide and was crystallised from dilute alcohol. It separated in pearly scales melting at 117° (Found: N=14·05. $C_{11}H_{14}O_2N_2$ requires N=13·60 per cent.).

This amide (6 grams) was condensed with sulphur monochloride (2 grams) in the presence of benzene (100 c.c.) as in the previous cases. The product was crystallised from a mixture of benzene and light petroleum, when it melted at 207—208° (Found: S=13·95. $C_{22}H_{26}O_4N_4S_2$ requires S=13·50 per cent.).

Methylmalonodimethylamide Disulphide, $S_2[CMe(CO{\cdot}NHMe)_2]_2$.

Methylmalonodimethylamide (Franchimont, *Rec. trav. chim.*, 1885, 4, 204), when condensed (10 grams) with sulphur monochloride (5 grams) in benzene (100 c.c.), yielded a crystalline product which melted at 200° after being washed with benzene (Found : S=18·72. $C_{12}H_{26}O_4N_4S_2$ requires S=18·28 per cent.).

Interaction of Ethyl Sodiocyanoacetate and Sulphur Monochloride.

Ethyl sodiocyanoacetate, prepared from 25 grams of ethyl cyanoacetate, was refluxed for one hour with sulphur monochloride (15 grams) and dry benzene (100 c.c.). The dark solution on evaporation left an oil which, when distilled under reduced pressure, yielded a solid. After crystallisation from ether, this melted at 117—118°, contained no sulphur and was identified as ethyl dicyanosuccinate (Found : N=12·76. Calc., N=12·50 per cent.).

Interaction of Ethyl Sodiomalonate and Sulphur Monochloride.

Ethyl sodiomalonate, prepared from 50 grams of the ester, was refluxed with sulphur monochloride (0·5 mol.) in the manner described in the last experiment. The product, after crystallisation from ether, was identified as ethyl ethanetetracarboxylate (Found : C=52·46; H=6·57. Calc., C=52·83; H=6·91 per cent.).

Interaction of Ethyl Cyanoacetate and Sulphur Monochloride.

Ethyl cyanoacetate (20 grams) was heated on a water-bath with sulphur monochloride (25 grams) and the product obtained on cooling was extracted from the sulphur produced by a large quantity of ether. The solid obtained after evaporation of the solvent was crystallised from benzene. It melted at 117—118° and was identified as ethyl dicyanosuccinate.

Interaction of Ethyl Malonate and Sulphur Monochloride.

This condensation was conducted like the preceding, excepting that heating on a sand-bath was necessary to complete the reaction. The solid product was extracted with benzene and crystallised from light petroleum until it melted at 57—58°. It was identified as ethyl ethylenetetracarboxylate. The same product was obtained when benzene was used as solvent and the product (an oil) subjected to distillation under reduced pressure.

Interaction of 1 : 1-*Dimethyl*cyclo*hexane*-3 : 5-*dione and Sulphur Monochloride.* 3 : 5 : 3′ : 5′-*Tetraketo*-4 : 4′-*bisdithio*-1 : 1 : 1′ : 1′-*tetramethyldi*cyclo*hexyl* 2 : 2′-*Disulphide* (Formula VII).

The ketone (5 grams) and sulphur monochloride (10 grams) were allowed to react in boiling benzene (100 c.c.). The solution on cooling was filtered and the solvent was allowed to evaporate. The residue was again dissolved in benzene and after the solvent had evaporated, crystallised from a mixture of benzene and light petroleum, when it softened at 110° and melted with decomposition at 150°. The molecular weight, determined by the cryoscopic method in benzene solution, was 472·5 (Found : S=40·93. $C_{16}H_{18}O_4S_6$ requires S=41·20 per cent. ; M=466).

Interaction of cyclo*Hexane*spirocyclo*hexane*-3 : 5-*dione and Sulphur Monochloride.* 1 : 1′-*Di*cyclo*hexane*spiro-3 : 5 : 3′ : 5′-*tetraketo*-4 : 4′-*bisdithiodi*cyclo*hexylene* 2 : 2′ : 6 : 6′-*Bisdisulphide* (Formula VIII).

The ketone (2 grams), after being thoroughly dried in the steam-oven for fifteen minutes, was heated under reflux with sulphur monochloride (3 grams) and dry benzene (100 c.c.). The product was isolated and purified in the same way as the preceding compound; it softened at 113° and melted and decomposed at 155°. The molecular weight, determined by the cryoscopic method in benzene solution, was 618 (Found : S=41·72. $C_{22}H_{24}O_4S_8$ requires S=42·10 per cent. ; M=608).

Interaction of cyclo*Pentane*spirocyclo*hexane*-3 : 5-*dione and Sulphur Monochloride.* cyclo*Pentane*spiro-3 : 5-*diketo*-4-*dithio*cyclo*hexane* (Formula VI).

The ketone (2 grams) was boiled for two hours with sulphur monochloride (3 grams) dissolved in benzene (50 c.c.). The product was isolated and purified as in the preceding cases; it softened at 114° and melted at 135°. The molecular weight, determined by the cryoscopic method in benzene solution, was 219 (Found : S=28·45. $C_{10}H_{12}O_2S_2$ requires S=28·07 per cent. ; M=228).

αγ-Disulphidoacetonedicarboxydianilide (Formula X).

The acetonedicarboxydianilide required for the purpose was prepared by the method of Besthorn and Garben (*loc. cit.*) and purified by crystallisation from benzene. The more soluble ethyl γ-phenylcarbamylacetoacetate was recovered as a by-product from the residues.

A mixture of the dianilide (4 grams), sulphur monochloride (4 grams), and dry benzene (100 c.c.) was heated under reflux for two hours. The solution became deep red and hydrogen chloride was immediately evolved. The liquid was allowed to cool and the golden-yellow, crystalline product collected and recrystallised from benzene, when it melted at 220°. The molecular weight, determined by the cryoscopic method in benzene solution, was 343 (Found: $N=8{\cdot}15$; $S=18{\cdot}41$. $C_{17}H_{14}O_3N_2S_2$ requires $N=7{\cdot}82$; $S=17{\cdot}87$ per cent.; $M=358$).

Ethyl γ-Phenylcarbamyl-αγ-bisdisulphidoacetoacetate (Formula IX).

Ethyl γ-phenylcarbamylacetoacetate (4 grams) and sulphur monochloride (5 grams) were heated under reflux with dry benzene (50 c.c.). The red solution was filtered and the solvent allowed to evaporate, the residue being repeatedly dissolved in benzene and precipitated by light petroleum until it was pure. When heated, it sintered at 115° and melted with decomposition at 156—157°. The molecular weight, determined by the cryoscopic method in benzene, was 393·5 (Found: $S=34{\cdot}69$. $C_{13}H_{11}O_3NS_4$ requires $S=34{\cdot}31$ per cent.; $M=373{\cdot}0$).

αγ-Disulphidoacetonedicarboxydi-p-*toluidide.*

Preparation of Acetonedicarboxydi-p-*toluidide.*—Acetonedicarboxylic ester (25 grams) and *p*-toluidine (17·5 grams) were heated together in a sealed tube at 120° for twenty-four hours. When the contents of the tube were poured into benzene (500 c.c.) the *toluidide* separated in beautiful crystals, which, after recrystallisation from benzene, melted at 169—170° (Found: $N=8{\cdot}25$. $C_{19}H_{20}O_3N_2$ requires $N=8{\cdot}64$ per cent.).

A mixture of the amide (6 grams), sulphur monochloride (5 grams), and dry benzene (100 c.c.) was heated under reflux for two hours. The product, being sparingly soluble in benzene, separated from the hot solution in brilliant, golden-yellow flakes which melted on recrystallisation at 216—217° (Found: $S=16{\cdot}14$. $C_{19}H_{18}O_3N_3S_2$ requires $S=16{\cdot}58$ per cent.).

αγ-Disulphidoacetonedicarboxydi-o-*toluidide.*

Preparation of Acetonedicarboxydi-o-*toluidide.*—This substance was prepared in the same way as the corresponding *p*-tolyl derivative, and on recrystallisation from benzene melted at 167° (Found: $N=8{\cdot}86$. $C_{19}H_{20}O_3N_2$ requires $N=8{\cdot}64$ per cent.).

The amide was heated with sulphur monochloride in the same way as the corresponding *p*-compound. The product was sparingly soluble in benzene, from which it separated in brilliant orange crystals melting at 225° with decomposition (Found: S=16·88. $C_{19}H_{18}O_3N_2S_2$ requires S=16·58 per cent.).

In conclusion, I have very great pleasure in recording my thanks to Prof. J. F. Thorpe, Dr. M. A. Whiteley, and Mr. C. K. Ingold for their keen interest throughout this work, and to the Chemical Society for a grant which has partly defrayed the expense of this investigation.

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CXXXVIII.—*An Improved Gas Combustion Furnace for Use in Organic Analysis.*

By THOMAS JOHNSON HEDLEY.

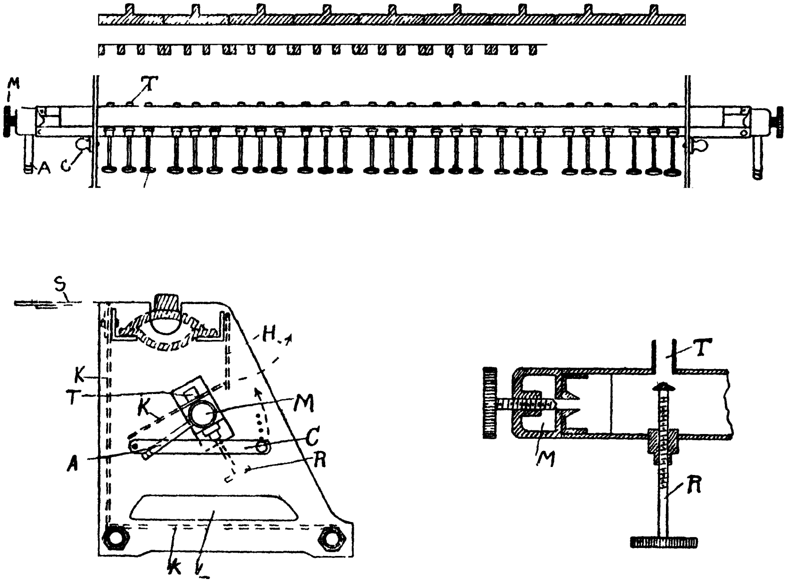
IN view of the extensive use of gas combustion furnaces in organic analysis, it is remarkable that little advance has been made in removing the following disadvantages possessed by the usual types, namely: non-portability, discomfort to the operator due to lack of protection from radiant heat, heavy gas consumption, unnecessarily slow heating and cooling, and high initial cost.

These disadvantages are obviated in the furnace shown in the following line-drawing.

A steel frame of light construction carries a number of trough tiles and covers in the channel formed by the two angle-iron stays which brace the top of the frame; the back and the base of the frame are covered with sheets of "uralite," and at the front a hinged screen of the same material protects the operator and allows of the inspection of the flames.

The multiple flame burner, which is of novel type, consists of a tube partitioned at the centre, each half being separately supplied with gas; individual flames are controlled by means of cone valves and may be turned down as low as desired or completely extinguished without any possibility of the whole burner "striking back."

The endplates of the frame are slotted to receive the burner, which rests upon a spring arm at each end, and its proximity to the underside of the furnace tiles is adjusted by elevating or depressing the arms.



Explanatory.

A, gas inlet ; C, spring arms (for adjusting height of burners) ; H, hinged screen ; K, K, K, fixed screens; L, lifting slots ; M, main gas regulators ; R, cone valves ; S, hot-tile shelf ; T, burner tubes.

Owing to the small bulk of the tiles, the temperature at any point of the furnace responds rapidly to alterations in the size of the flames, and the non-effective absorption of heat, and therefore the consumption of gas, is reduced to a minimum.

The complete furnace weighs less than thirty pounds and the cost of construction is less than half that of any existing type of gas combustion furnace.

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CXXXIX.—*The Action of the Grignard Reagent on certain Tervalent Organo-iodo-compounds.*

By Harry Hepworth.

Lachmann (*Ber.*, 1897, **30**, 887) studied the action of zinc ethyl on iodobenzene dichloride, doubtless in the hope of isolating a mixed aliphatic aromatic iodonium compound. The reaction was very vigorous, but no iodonium compound was produced.

Willgerodt (*Ber.*, 1897, **30**, 56; 1898, **31**, 915) investigated the action of mercury phenyl and mercuric phenyl chloride on iodochlorides, both in the presence and the absence of water. Three compounds were formed, diphenyliodonium chloride, mercuric phenyl chloride and a double compound of diphenyliodonium chloride with mercuric chloride. Mercury ethyl was substituted for mercury diphenyl in the hope of obtaining a phenylethyliodonium chloride, but this aspiration was not realised, the products of reaction being ethyl chloride, iodobenzene, and either mercuric ethyl chloride or mercuric chloride.

In the experiments described in this paper the action of magnesium, magnesium ethyl bromide, and magnesium phenyl bromide on iodobenzene dichloride, iodosobenzene, iodoxybenzene, and the corresponding toluene compounds is described. In the first instance, the action of magnesium powder on iodobenzene dichloride and *p*-iodotoluene dichloride was investigated. The addition of a crystal of iodine to the ethereal suspension of the dichloride, and a little magnesium powder catalyses the reaction, which proceeds vigorously, the products being magnesium chloride, benzene or toluene, iodobenzene or *p*-iodotoluene, and a little diphenyl. The reaction is best represented as follows :

$$PhICl_2 + 2Mg = MgPhI + MgCl_2$$
$$PhICl_2 + Mg = PhI + MgCl_2,$$

both reactions taking place concurrently.

Iodobenzene and diphenyl are the principal products of the reaction between magnesium phenyl bromide and iodobenzene dichloride, whilst diphenyliodonium chloride is formed in small quantities. The principal reaction is represented by the equation :

$$PhICl_2 + 2MgPhBr = MgCl_2 + MgBr_2 + Ph{\cdot}Ph + PhI$$
$$PhICl_2 + 3MgPhBr = MgCl_2 + MgBr_2 + MgIBr + 2Ph{\cdot}Ph,$$

and to a smaller extent :

$$PhICl_2 + MgPhBr = Ph_2ICl + MgClBr.$$

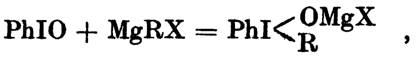
Similar compounds were obtained by the action of magnesium phenyl bromide on *p*-iodotoluene dichloride.

Magnesium alkyl haloids and iodobenzene dichloride gave the corresponding paraffin hydrocarbons and alkyl derivatives of benzene. No iodonium bases were formed in these reactions.

$$PhICl_2 + 3MgRX = PhR + R_2 + 2MgXCl + MgXI.$$

Corresponding compounds were obtained from *p*-iodotoluene dichloride.

The reaction between Grignard compounds and iodoso-compounds in suspension in ether and toluene is very slow. Magnesium ethyl bromide and iodosobenzene gave iodobenzene only, whilst magnesium phenyl bromide gave iodobenzene and a little diphenyl-iodonium hydroxide. The normal reaction;



$$PhIO + MgRX = PhI<^{OMgX}_{R} \quad ,$$

only takes place even partly in the case of magnesium phenyl bromide. Magnesium alkyl haloids reduce iodoso-compounds to iodo-compounds.

In contrast with the iodoso-compounds, the iodoxy-compounds react readily with organo-magnesium compounds, but in all cases the latter act as reducing agents, the original iodo-compounds being regenerated and no iodonium bases being formed.

It will thus be seen that whilst small quantities of diphenyl-iodonium and phenyl-*p*-tolyliodonium bases may be obtained by the action of magnesium phenyl bromide on the corresponding iodo-dichlorides and iodoso-compounds, no indications of mixed aliphatic aromatic iodonium bases have been obtained by the action of magnesium alkyl haloids on the same compounds, and that these organo-metallic compounds simply function as reducing agents to iodoso- and iodoxy-compounds.

In view of the fact that the chlorine atoms in iodo-dichlorides are ionisable and readily removed, it is suggested that the formula (R.I.) .....Cl_2 represents their behaviour better than the older formula.

EXPERIMENTAL.

Action of Magnesium Powder on Iodobenzene Dichloride and p-*Iodotoluene Dichloride.*

Iodobenzene dichloride was prepared by leading a current of dry chlorine into an ice-cold solution of iodobenzene in dry chloroform according to the method of Willgerodt (*J. pr. Chem.*, 1886, [ii], **33**, 154), whilst *p*-iodotoluene dichloride was prepared in a similar manner from *p*-iodotoluene. Willgerodt (*Ber.*, 1893, **26**,

357) states that *p*-iodotoluene dichloride deposited from a chloroform solution melts at 85°, but the compound obtained by the author melted at 104—105°. This is in close agreement with the melting point obtained by Ortoleva (*Gior. Soc. Sci. Nat. Econ.*, 1900, 23), who found that *p*-iodotoluene dichloride melted at 105—106° independent of the solvent from which it was crystallised.

A preliminary experiment showed that iodobenzene dichloride and *p*-iodotoluene dichloride only underwent very slight decomposition when heated in ethereal suspension for several hours.

On adding a trace of magnesium powder to an ethereal suspension of 5 grams of *p*-iodotoluene dichloride in 30 c.c. of dry ether, and heating on a water-bath, no evident reaction took place. The mixture was allowed to cool and a minute crystal of iodine added, when reaction proceeded in the cold and the ether ultimately boiled. Magnesium powder (1·25 grams) was added in small quantities from time to time and the mixture was stirred continuously. After about two hours, when about half the magnesium had been added, the reaction became very feeble, and the mixture was warmed on a water-bath. The rest of the magnesium was added during the course of an hour and the heating continued; at the end of five hours, a little unchanged magnesium was still present. The mixture was allowed to settle, the clear superincumbent ethereal solution filtered through dry asbestos, and the residue washed four times with 20 c.c. of dry ether. On adding water to the residue, there was a slight momentary reaction, thus showing that a little magnesium *p*-tolyl iodide was still present. The aqueous solution was filtered and found to contain 1·3 grams of magnesium chloride.

The ethereal solution was decomposed with water, when a vigorous reaction ensued. The ethereal layer was separated and the aqueous portion extracted twice with ether. After drying and distillation of the ether, 1·1 grams of toluene (b. p. 109—110°) and 1·2 grams of *p*-iodotoluene (m. p. 35°; b. p. 210—212°) were obtained by fractionation. The *p*-iodotoluene was separated from traces of *pp'*-ditolyl by crystallisation from alcohol.

In a similar experiment with 5·5 grams of iodobenzene dichloride and 1·3 grams of magnesium powder, 1·2 grams of magnesium chloride, 1·1 grams of iodobenzene (b. p. 187—189°), and traces of benzene and diphenyl were obtained.

Action of Magnesium Ethyl Bromide and Magnesium Phenyl Bromide on Iodobenzene Dichloride and p-*Iodotoluene Dichloride.*

A preliminary experiment showed that magnesium methyl iodide reacted vigorously with iodobenzene dichloride with the evolution of a gas. In an experiment in which excess of magnesium methyl iodide in anisole solution was added to 0·1 gram of iodobenzene dichloride in 10 c.c. of anisole, 7 c.c. of ethane were collected over dry mercury.

Iodobenzene dichloride (5·5 grams) was added, a little at a time, to a solution of magnesium ethyl bromide prepared from 0·8 gram of magnesium, 3·4 grams of ethyl bromide, and 50 c.c. of dry ether. A vigorous reaction ensued, the mixture became homogeneous and the ether boiled, but after the addition of about 3 grams of the iodo-chloride very little further reaction took place. After an hour much magnesium chloride had separated. The mixture was kept overnight and then cautiously decomposed with ice-cold water. After extraction, removal of the ether, and repeated fractionation, 0·9 gram of ethylbenzene (b. p. 134—136°) and 1·2 grams of iodobenzene (b. p. 187—189°) were obtained. The identity of the product, b. p. 134—136°, with ethylbenzene was further established by its oxidation with permanganate to benzoic acid. No iodonium base was found in the aqueous solution after decomposition of the product with water, and it is evident that insufficient magnesium ethyl bromide had been employed to react with the whole of the iodobenzene dichloride.

In a second experiment in which 2·5 mols. of magnesium ethyl bromide were employed, the sole products of reaction were ethylbenzene and a little iodobenzene.

Experiments were carried out in which magnesium and ethyl bromide were added from time to time to a well-stirred emulsion of iodobenzene dichloride and ether cooled in ice, but again no iodonium base was formed, the principal product being ethylbenzene. With 3·5 mols. of magnesium ethyl bromide, ethylbenzene was almost the sole product of reaction.

In similar experiments with *p*-iodotoluene dichloride and magnesium ethyl bromide, *p*-ethyltoluene and *p*-iodotoluene were the principal products, whilst a gas, probably butane, was given off. The aqueous solution obtained on decomposing the preliminary products with water contained no organic matter.

With magnesium phenyl bromide and iodobenzene dichloride, diphenyl (m. p. 70·5°; b. p. 254°) and iodobenzene (b. p. 188°) were formed, whilst the filtered aqueous solution obtained after decomposing the product of reaction with water gave only a little diphenyliodonium iodide on the addition of an aqueous solution of potassium iodide.

Similar results were obtained with magnesium phenyl bromide and *p*-iodotoluene dichloride. A small quantity of phenyl-*p*-tolyliodonium iodide was obtained on treating the aqueous solution, obtained on decomposing the product with water, with an aqueous solution of potassium iodide.

Action of Magnesium Ethyl Bromide and Magnesium Phenyl Bromide on Iodosobenzene and p-*Iodosotoluene.*

Iodosobenzene and *p*-iodosotoluene were obtained by the action of an aqueous solution of sodium hydroxide on the corresponding iodo-dichlorides, as described by Willgerodt (*Ber.*, 1892, **25**, 3494).

Four and a half grams of iodosobenzene were added to an ethereal solution of magnesium ethyl bromide prepared from 0·8 gram (1·5 mols.) of magnesium, 3·6 grams of ethyl bromide, and 30 c.c. of dry ether. There was no evident reaction in the cold and the iodosobenzene did not go into solution. After heating on the water-bath for three hours, the bulk of the iodosobenzene still remained undissolved. The greater part of the ether was evaporated and 50 c.c. of toluene, which had been dried over sodium and distilled over phosphoric oxide, were added. The flask was now heated on a sand-bath for two days, when rather less than half of the iodosobenzene reacted. On decomposing the mixture with water, a vigorous reaction ensued. The contents of the flask were extracted four times with ether, and after removal of the ether about 1 gram of iodobenzene (b. p. 186—189°) was obtained. The aqueous portion containing iodosobenzene and magnesium hydroxide in suspension was filtered, but the clear filtrate contained no iodonium base. The residue contained no organic matter other than iodosobenzene.

In a similar experiment in which 4·5 grams of iodosobenzene, 0·8 gram (1·5 mols.) of magnesium and 5 grams of bromobenzene were used, 1·5 grams of iodobenzene and 3 grams of diphenyl were obtained, whilst a little diphenyliodonium iodide was obtained by treating the aqueous solution obtained on decomposing the reaction product with water, with an aqueous solution of potassium iodide.

Similar results were obtained on treating *p*-iodosotoluene with magnesium ethyl bromide. With magnesium phenyl bromide, a small quantity of phenyl-*p*-tolyliodonium iodide was obtained.

Action of Magnesium Ethyl Bromide and Magnesium Phenyl Bromide on Iodoxybenzene and p-*Iodoxytoluene.*

Iodoxybenzene and *p*-iodoxytoluene were prepared from the corresponding iodoso-compounds by distillation in steam in the usual manner.

p-Iodoxytoluene (2·25 grams) was added a little at a time to a solution of magnesium ethyl bromide prepared from 1·5 grams (3 mols.) of magnesium, 6·5 grams of ethyl bromide, and 30 c.c of dry ether, the whole being kept at room temperature. A vigorous reaction ensued, and on warming on the water-bath for half an hour almost the whole of the iodoxybenzene went into solution. The flask was kept overnight at room temperature, when an oil was observed at the bottom of the flask. The product was decomposed by ice-cold water and extracted three times with ether. After drying and removing the ether, 1·8 grams of iodobenzene (b. p. 186—188°) were obtained. The aqueous solution contained no iodonium base and the residue insoluble in water contained no organic matter.

Magnesium phenyl bromide reacted with iodoxybenzene much less readily, and after warming for eight hours on the water-bath, a little unchanged iodoxybenzene still remained. The sole products of reaction were diphenyl and iodobenzene and no iodonium base was present in the aqueous solution.

Similar results were obtained by the action of magnesium ethyl bromide and of magnesium phenyl bromide on *p*-iodoxytoluene.

The author is indebted to the Research Committee of Messrs. Nobel's Explosives Co., and particularly to Mr: Rintoul, for the facilities accorded him in carrying out this investigation.

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CXL.—*Accelerated Formation of Magnesium Alkyl and Aryl Haloids.*

By HARRY HEPWORTH.

IN carrying out syntheses with the aid of the Grignard reagent it is customary to employ ethyl ether as the solvent medium in which the required magnesium alkyl or aryl haloid is prepared, and for a considerable period the ethers were the only class of compounds which were known to catalyse the formation of magnesium alkyl haloids from their components. From the initial analysis by Blaise (*Compt. rend.*, 1901, **132**, 839) it was concluded that these etherates were best represented by the formula $RMgX,Et_2O$. In view of the fact that Grignard showed in his dissertation (L'Univ. de Lyon, 1901) that the whole of the ether could not be removed from the compound MgMeI,Et_2O by heating for several days in a vacuum, Baeyer and Villiger (*Ber.*, 1902, **35**, 1201) regarded this compound as a true oxonium compound, ${}^{Et}_{Et}\!>\!O\!<\!{}^{MgMe}_{I}$. This structure admits of isomerism, and Tschelinzeff (*Compt. rend.*, 1907, **144**, 88) claimed to have obtained evidence of such isomerism. Grignard, however, has claimed (*Bull. Soc. chim.*, 1907, [iv], **1**, 256) that his formula ${}^{Et}_{Et}\!>\!O\!<\!{}^{MgI}_{Me}$ (*Compt. rend.*, 1903, **136**, 1260), also admits of the existence of isomerides, since the two additional valencies of the oxygen atom have not the same value as the original two.

In 1904, Tschelinzeff (*Ber.*, 1904, **37**, 4534) came to the conclusion that the ether plays the part of a catalyst, forming an additive compound with the alkyl haloid, which subsequently reacts with magnesium to form magnesium alkyl haloid with regeneration of the original ether, and further, that the ether may be replaced by tertiary amines. Somewhat later (*Ber.*, 1908, **41**, 646), he claimed to have isolated "aminates" of the general formula R_3N,MgRX and "amine etherates" of the type R_3N,MgRX,Et_2O. The use of tertiary amines instead of ethers has not met with much success in the author's experience. Several investigators have, however, shown that tertiary bases react with magnesium alkyl haloids in the presence of ether to form double compounds containing the base, magnesium alkyl haloid and sometimes ether also (Sache, *Ber.*, 1904, **37**, 3088; Oddo, *Atti R. Accad. Lincei*, 1904, [v], **13**, 106; Houben, *Ber.*, 1905, **38**, 3017; Senier, P., 1905, **21**, 327; T., 1905, **87**, 1469).

In the course of their investigation on oxonium compounds, Pickard and Kenyon (T., 1906, **89**, 262) found that tribenzylphosphine oxide may replace ether in the formation of magnesium alkyl haloids, and succeeded in obtaining a compound,

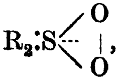
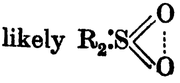
$$2(C_7H_7)_3PO,CH_3\cdot MgI,$$

in the crystalline condition. It may also be pointed out that these authors prefer to write the formulæ of the Grignard reagents as Et_2O . . . MgRX in accordance with Werner's views of valency (*Annalen*, 1902, **322**, 296).

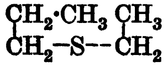
It has now been found that the alkyl sulphides accelerate the formation of magnesium methyl iodide, but not to such an extent as ether. Double compounds containing alkyl sulphide and magnesium methyl iodide are formed, but these have not been obtained in the crystalline condition. Similar results have been obtained with iodobenzene, but the reaction is very much slower than with methyl iodide. In a similar way, it was found that diethyl selenide and dimethyl telluride accelerated the formation of magnesium methyl iodide to about the same extent as diethyl sulphide, but that all these compounds are less effective than ethyl ether.

If the accelerating action of ether is to be explained on the grounds that the oxygen atom has a tendency to become quadrivalent, and that the accelerating influence is to be measured by the relative stability of these oxonium compounds, then it would be expected that the dialkyl sulphides, selenides, and tellurides would catalyse the reaction in ascending order of magnitude. The results obtained show that the capability to form compounds of higher valency, whilst it may be the initial cause of the catalysing action, has very little effect on the speed of the reaction, and that ether is unique among these compounds as regards its marked catalytic action.

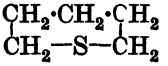
Experiments were now carried out in a similar manner in order to ascertain if the simple sulphoxides exerted a catalytic influence on the formation of magnesium methyl iodide. For this purpose, diphenyl sulphoxide and di*iso*amyl sulphoxide were prepared, and it was found that both these compounds were catalysts and that the double compounds formed were moderately soluble in hot benzene, but, on cooling, were deposited in an amorphous condition. From an estimation of the magnesium and the iodine content of these compounds, they would appear to conform with the general formula $2R_2SO,MgMeI$, but as the compounds were not obtained in the crystalline form, the results are not convincing. It is, however, evident that the sulphoxides are in this respect comparable with the phosphine oxides (Pickard and Kenyon, *loc. cit.*). The catalysing action of the sulphoxides is rather more pronounced than that of the sulphides, and it is suggested that this is due to the presence of an oxygen atom in the former compounds.

Similar experiments carried out with dimethylsulphone and diphenylsulphone showed that these compounds exerted no catalysing action on the formation of magnesium methyl iodide. Pickard and Kenyon (T., 1907, **91**, 896) have shown that whilst diphenyl sulphoxide readily forms additive compounds, diphenylsulphone does not do so, and have suggested the formula  $R_2{:}S\begin{matrix}\nearrow O\\ \cdots\ |\\ \searrow O\end{matrix}$, or less likely  $R_2{:}S\begin{matrix}/\!\!/ O\\ \vdots\\ \backslash\!\!\backslash O\end{matrix}$ (where the dots represent subsidiary valencies) for the sulphones. Since the sulphones are stable, neutral compounds, in which both oxygen atoms are firmly attached to sulphur, the author prefers the latter formula rather than the former, which portrays the sulphones as peroxides. The inability of the sulphones to catalyse the formation of magnesium methyl iodide may be due to the influence of the additional oxygen atom, whereby the greater part of the residual affinity of each oxygen atom is mutually compensated.

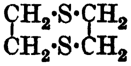
It was now decided to prepare a series of heterocyclic sulphur compounds in order to ascertain whether such substances exerted any catalysing influence, and whether any relationship existed between the structure of these compounds, containing "unsaturated" sulphur atoms, to which a large amount of residual affinity is attributed, and the property of catalysing the formation of magnesium methyl iodide. For this purpose the following substances were prepared and examined :



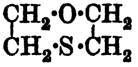
Ethyl *n*-propyl sulphide.



Pentamethylene sulphide.

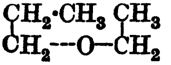


1 : 4-Dithian.

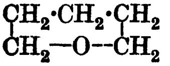


1 : 4-Thioxan.

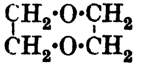
For comparative purposes, the following compounds containing oxygen in place of sulphur were prepared and examined :



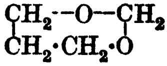
Ethyl *n*-propyl ether.



Pentamethylene oxide.



1 : 4-Dioxan.



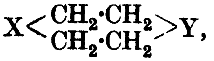
1 : 3-Dioxan.

The method employed was to introduce 1 gram of the substance, 0·3 gram of magnesium, and 2 grams of methyl iodide into 50 c.c. of dry benzene, and to heat the mixture under reflux on a water-bath. A series of experiments was carried out each time, the series always including two blank experiments, with and without the addition of 1 gram of dry ether. It was found to be comparatively easy to ascertain when reaction had definitely set in, and the vigour with which decomposition ensued on the addition of ice-cold water at a constant rate gave a further confirmation as to the extent to which reaction had occurred. The results are more uniform in the case of the sulphur than the oxygen compounds, because the former react more slowly. The results obtained were as follows :

(1) It was found that the open-chain compounds, ethyl *n*-propyl ether and ethyl *n*-propyl sulphide, reacted more readily than pentamethylene oxide and sulphide respectively, from which it is evident that ring formation diminishes the catalytic activity of these compounds.

(2) 1 : 4-Dithian and 1 : 4-dioxan are more active than penta-

methylene sulphide and oxide respectively, whilst 1 : 4-dithian is almost as active as 1 : 4-dioxan, but both are much less active than ethyl *n*-propyl sulphide and oxide respectively. The marked unsaturation of 1 : 4-dithian and 1 : 4-dioxan may be attributed to the presence of two sulphur and two oxygen atoms respectively in the 1 : 4-position (Clarke, T., 1912, **101**, 1801). That the two oxygen atoms in 1 : 4-dioxan exert a mutual influence, the effect of which is to augment the basic function, has been shown by Faworsky (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 741), Paternò and Spallino (*Atti R. Accad. Lincei*, 1907, [V], **16**, 187) and others, who observed that 1 : 4-dioxan readily yields salts with sulphuric acid, bromine, iodine, picric acid, and mercuric chloride, whilst the corresponding open-chain compound, αβ-dimethoxyethane, is neutral. The marked basic function of 1 : 4-dioxan does not confer any increased catalytic activity over ethyl *n*-propyl ether in the formation of magnesium methyl iodide.

(3) 1 : 4-Thioxan is more active than 1 : 4-dithian, its activity being almost equal to that of 1 : 4-dioxan. This again shows that the oxygen compounds are more active than the corresponding sulphur compounds, and that the oxygen atom is unique in its marked catalysing action. Smiles (T., 1909, **95**, 994) has shown that the sulphur atom in 3 : 5-diethoxy-1 : 4-thioxan is sluggish in its chemical functions, whilst Clarke (*loc. cit.*) has found that the velocity of reaction of bromoacetophenone with 1 : 4-thioxan is much slower than with pentamethylene sulphide and 1 : 4-dithian. If the catalysing action of 1 : 4-thioxan in the formation of magnesium alkyl haloids were due solely to the tendency of the oxygen and sulphur atoms to become quadrivalent, then it would be expected to be much less active than 1 : 4-dithian, especially since Clarke (*loc. cit.*) has shown that in compounds of the type  $X{<}{\begin{smallmatrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{smallmatrix}}{>}Y$, where X and Y are both sulphur or both oxygen atoms, the effect of the mutual influence is to increase the reactivity, whilst if X and Y are sulphur and oxygen respectively, the reactivity is depressed.

(4) No difference in reactivity could be detected between 1 : 3-dioxan and 1 : 4-dioxan. The former compound only forms an unstable picrate and yields a crystalline double compound with mercuric chloride, whilst 1 : 4-dioxan is much more basic. This again indicates that the catalytic activity is not due solely to the unsaturated nature of the oxygen atoms in these compounds. Both compounds are much less active in their catalysing action in the formation of magnesium methyl iodide than is ethyl *n*-propyl ether.

It is not proposed to deal here with the voluminous literature which has been published on the part played by ether in the formation of Grignard reagents. Although Tingle (*Amer. Chem. J.*, 1907, **37**, 483) has shown that ether is not essential, provided sufficient time is allowed, and Spencer (T., 1908, **93**, 68) has shown that magnesium and phenyl iodide react at the boiling point of the latter, yet ether does enormously accelerate the formation of Grignard compounds, and none of the sulphur compounds examined during this investigation is so effective. Tschelinzeff's view (*Ber.*, 1904, **37**, 4534) that a mere trace of ether is sufficient, has not been substantiated in the author's experience, and it should be pointed out that the fact that ether is a catalyst does not necessarily exclude the formation of "oxonium" compounds during the course of the reaction. Very little reliance can be placed on the analysis of these oxonium compounds, because, with the exception of the double compound formed between amyl ether and magnesium methyl iodide (Zerewitinoff, *Ber.*, 1908, **41**, 2244), and that between tribenzylphosphine oxide and magnesium methyl iodide (Pickard and Kenyon, *loc. cit.*), the majority of these compounds have only been obtained as amorphous solids. The results obtained in this paper show that ether is unique in its catalytic action, and that sulphur, selenium, and tellurium compounds, which show an increasing tendency to become quadrivalent, do not catalyse the formation of magnesium alkyl and aryl haloids to such an extent as the corresponding oxygen compounds.

EXPERIMENTAL.

Diethyl Sulphide.—This was prepared by the action of an excess of concentrated aqueous sodium sulphide on sodium ethyl sulphate. After removal of ethyl mercaptan by shaking with 40 per cent. aqueous potassium hydroxide, the product was dried over sodium and distilled over phosphoric oxide; b. p. 92—92·5°, d_4^{21} 0·8367.

Diisoamyl sulphide was prepared in a similar manner from potassium amyl sulphate and potassium sulphide; b. p. 215°, $d_4^{20^\circ}$ 0·8433.

Ethyl n-*propyl sulphide* was prepared by the action of *n*-propyl bromide on an alcoholic solution of the sodium salt of ethyl mercaptan (Strömholm, *Ber.*, 1900, **33**, 830). After distillation in steam, the mercurichloride was precipitated as a heavy oil by the addition of an excess of dilute mercuric chloride solution. The oil, after being washed with water, was decomposed by distillation with aqueous sodium sulphide solution. The sulphide was then dried by distillation over freshly fused potassium hydroxide, and repeatedly distilled over metallic sodium; b. p. 116—117°, $d_{4^\circ}^{20^\circ}$ 0·8446.

Pentamethylene Sulphide.—Thirty grams of αε-dichloropentane, prepared by Braun's method (*Ber.*, 1904, **37**, 2918) were heated for four hours under reflux with a dilute alcoholic solution of about twice the calculated quantity of potassium sulphide. After distillation in steam, the product was precipitated as the mercurichloride, which was well washed with water and decomposed by distillation with aqueous sodium sulphide solution. The separated oil was distilled over freshly fused potassium hydroxide and then over sodium; b. p. 141—142° (Braun and Wallach, *Festschrift*, 1909, 381), d_4^{20} 0·98379.

1 : 4-*Thioxan.*—This compound was first obtained by Clarke (T., 1912, **101**, 1806) by the action of dilute alcoholic potassium sulphide on ββ′-di-iodoethyl ether.

The thioxan used in this investigation was prepared from thiodiglycol (v. Meyer, *Ber.*, 1886, **19**, 3259) as follows: Thiodiglycol (30 grams) and concentrated sulphuric acid (1·25 grams) were heated together, when a moderate reaction ensued at 180° and the distillate obtained separated into two layers. The lower layer was removed and purified by conversion into the mercurichloride (m. p. 170°) and subsequent decomposition by potassium sulphide, followed by repeated distillation over freshly fused potassium hydroxide and sodium. The product boiled constantly at 148°; d_4^{20} 1·11744.

Diphenyl Sulphoxide.—This was prepared by the action of magnesium phenyl bromide on benzenesulphonyl chloride. The details of this preparation will be given in a later communication. After two crystallisations from benzene, the product melted at 69·8°.

Diisoamyl sulphoxide was obtained by the oxidation of di*iso*amyl sulphide, in acetone, with 30 per cent. hydrogen peroxide (Smiles, T., 1908, **93**, 1833). After crystallisation from light petroleum, the product melted at 35°.

Diphenylsulphone was obtained by the action of benzene on benzenesulphonyl chloride in the presence of aluminium chloride (Beckurts and Otto, *Ber.*, 1878, **11**, 2066). After recrystallisation from benzene, it melted at 128° and boiled at 230°/17 mm.

Dimethylsulphone was prepared by the action of fuming nitric acid on dimethyl sulphoxide nitrate. After removal of the greater part of the nitric acid by heating on the water-bath, the syrupy mixture was solidified by cooling in a freezing mixture, pressed, crystallised from water, and the product dried in a vacuum over potassium hydroxide and phosphoric oxide; m. p. 109°, b. p. 238—240°.

Ethyl n-*Propyl Ether.*—Small pieces of metallic sodium were added to pure *n*-propyl alcohol until sodium *n*-propoxide began to separate. Ethyl iodide, equivalent to the sodium used, was then added and the mixture heated under reflux for eight hours on a water-bath. On distillation, the fraction, b. p. 62—67°, was collected and repeatedly boiled with sodium until no further action took place. The pure ether distilled at 63° (Brühl, *Annalen,* 1880, **200**, 177).

Pentamethylene Oxide.—Twenty grams of $\alpha\epsilon$-dibromopentane, prepared and purified by Braun's method (*Ber.*, 1904, **37**, 3210; 1905, **38**, 2339), were converted into pentamethylene oxide by Clarke's method (T., 1912, **101**, 1802). After being dried with potassium hydroxide and sodium, it distilled at 87—88°.

1 : 4-*Dioxan* was prepared by heating a 4 per cent. solution of concentrated sulphuric acid in ethylene glycol on an oil-bath, according to the directions of Faworsky (*loc. cit.*). The distillate, which contained much acetaldehyde, was saturated with potassium hydroxide, the separated liquid distilled and repeatedly boiled under reflux with silver oxide. It was found necessary to treat the product repeatedly with silver oxide in order to remove the last traces of acetaldehyde. After separation and repeated distillation over freshly fused potassium hydroxide followed by distillation over sodium, a clear product, b. p. 101·5°, was obtained, which was free from aldehydes.

1 : 3-*Dioxan* was obtained from trimethylene glycol and trioxymethylene according to the method of Clarke (*loc. cit.*). After being repeatedly treated with silver oxide to remove aldehydes, a clear, colourless liquid, b. p. 105°, was obtained.

The author is gratefully indebted to the late Dr. Vernon for the gift of a small quantity of dimethyl telluride.

He is also indebted to the Research Committee of Messrs. Nobel's Explosives Company, Limited, and particularly to Mr. Rintoul, for the facilities accorded him in carrying out this investigation.

THE RESEARCH LABORATORIES,
STEVENSTON, N.B.

[*Received, May* 13*th*, 1921.]

CXLI.—*Aminoacylcholine Esters. Part I. Glycylcholine.*

By HAROLD WARD DUDLEY.

THE wide distribution of choline in the animal and vegetable kingdoms has led in recent times to a recognition of its importance in biological chemistry. Pharmacologically, this substance and its derivatives are very interesting. Acetylcholine, for instance, is an extraordinarily potent drug, exhibiting its action on the frog's heart in a dilution of 1 : 1000 millions.

It appeared, therefore, of interest to prepare and examine the properties of the esters of choline with the naturally occurring amino-acids, and this paper deals with the first compound of the series, glycylcholine.

A simple and direct method of obtaining this substance was found. It consisted in mixing glycyl chloride hydrochloride and choline chloride in the form of fine powders and heating at 100° in a vacuum. Hydrogen chloride gas was evolved with formation of glycylcholine, which was isolated as the platinichloride, from which the hydrochloride of glycylcholine chloride was obtained. The yield, considering the nature of the reaction, is fair, the average of a number of preparations being 56 per cent. of the theoretical.

Nothnagel (*Arch. Pharm.*, 1894, **232**, 266), in describing the preparation of acetylcholine, notes that after decomposing the gold salt with hydrogen sulphide, and removing the excess of the latter by heating, the acetylcholine is hydrolysed, for, on adding chloroplatinic acid to the filtrate, choline platinichloride separates out. Accordingly Ewins and others have decomposed acetylcholine platinichloride by adding to its solution in water potassium chloride, evaporating to dryness in a vacuum, and extracting the residue with absolute alcohol, in which acetylcholine chloride is readily soluble.

The first isolation of the hydrochloride of glycylcholine chloride was made by this method. It proved to be very laborious, since the substance is not soluble in absolute alcohol. After evaporating an aqueous solution of the platinichloride with the amount of potassium chloride theoretically required, the glycylcholine chloride hydrochloride was extracted with many washings of hot 98 per cent. alcohol. But this was unnecessary. It was found possible to decompose the platinichloride with hydrogen sulphide, to remove the excess of the latter from the filtrate and to concentrate the solution by distillation in a vacuum at a low temperature, without any perceptible hydrolysis of the glycylcholine occurring. It seems possible that this method may be applicable to acetylcholine, for there does not appear to be any particular reason why the ester linking of glycylcholine should be more stable than that of acetylcholine.

The action of glycyl chloride hydrochloride on free choline was tried, but proved to be complicated, and was not further studied.

Choline is usually described as a colourless syrup, which, being strongly basic, absorbs carbon dioxide from the air, and is thereby transformed into the crystalline carbonate. Griess and Harrow

(*Ber.*, 1885, **18**, 717), however, report that they obtained the free base as hygroscopic crystals; but Guggenheim ("Die Biogenen Amine," p. 68) expresses doubt as to whether their substance was not in reality the carbonate. It is worthy of note that in the course of this work free choline was readily obtained as a solid, crystalline, very hygroscopic mass under conditions precluding the formation of carbonate. A short description of its preparation is appended.

The pharmacological behaviour of glycylcholine and other members of this series of compounds will be discussed elsewhere at a later date.

EXPERIMENTAL.

Glycylcholine Platinichloride, $NMe_3Cl{\cdot}C_2H_4O{\cdot}CO{\cdot}CH_2{\cdot}NH_2,HCl,PtCl_4,H_2O$.

Glycyl chloride hydrochloride was prepared without difficulty by Fischer's method, a very fine, snow-white powder, which gave a satisfactory analysis, being obtained. It was stored in a vacuum desiccator over phosphoric oxide. Choline chloride was obtained as a fine, white, crystalline powder by dissolving it in a small quantity of absolute alcohol and pouring the solution into a large volume of pure dry ether, at the same time stirring vigorously. The finely divided, precipitated choline chloride was filtered off rapidly and kept in a vacuum desiccator over phosphoric oxide. Equal amounts (0·3 gram) of the two dry powders were mixed in a test-tube, which, after being evacuated with the aid of a water-pump, was half immersed in a boiling-water-bath and heated for about six hours. The powder shrank and developed a faintly yellow tinge. After being allowed to cool, the product was digested with about 5 c.c. of absolute alcohol to decompose any unchanged glycyl chloride hydrochloride and to remove choline chloride, filtered, the residue dissolved in 10 c.c. of 50 per cent. alcohol, and the solution filtered. To the filtrate were added 15 c.c. of a 5 per cent. aqueous solution of chloroplatinic acid. An immediate turbidity was produced and the platinum salt was rapidly deposited in clusters of orange needles. After remaining over-night at about 2°, the platinichloride was filtered off, washed with a little 50 per cent. alcohol, and dried on porous plate in the air: yield 0·68 gram. The salt gave correct figures on analysis, without further purification, and was found to contain 1 mol. of water of crystallisation. It melted at 236—238° (uncorr.) with vigorous decomposition (Found: loss at 122° = 2·83; Pt in anhydrous salt = 34·15. $C_7H_{18}O_2N_2Cl_6Pt,H_2O$ requires $H_2O = 3{\cdot}06$. $C_7H_{18}O_2N_2Cl_6Pt$ requires Pt = 34·2 per cent.).

This platinichloride is insoluble in absolute alcohol, but is moderately soluble in water.

Decomposition of Glycylcholine Platinichloride by Hydrogen Sulphide.

The platinichloride (0·1890 gram) was dissolved in 30 c.c. of water at 38°, and hydrogen sulphide was passed through the solution, which was allowed to cool to room temperature, until all the platinum had been removed. After being filtered, the clear, colourless solution was concentrated to about 3 c.c. in a vacuum at 30—35°, made up to 8 c.c. with absolute alcohol, and 5 c.c. of a 5 per cent. aqueous solution of chloroplatinic acid were added; 0·1311 gram of platinichloride was recovered. This melted at 236—238° and gave correct analytical figures for glycylcholine platinichloride (Found: $H_2O=2·55$; Pt in anhydrous salt$=34·3$ per cent.).

Glycylcholine Chloride Hydrochloride.

The platinichloride (0·453 gram) was dissolved in 70 c.c. of water at 37°, the platinum precipitated by hydrogen sulphide, and the clear filtrate evaporated in a vacuum (water-bath at 30—35°). When the volume was about 4 c.c., alcohol was added and the solution again evaporated in a vacuum. This process was repeated and the solution finally evaporated to dryness. The hydrochloride is a hygroscopic, white, crystalline substance, very soluble in water, from which it crystallises in prismatic needles. It is insoluble in absolute alcohol.

Glycylcholine Aurichloride, $NMe_3Cl·C_2H_4O·CO·CH_2·NH_2,HCl,2AuCl_3$.

Glycylcholine platinichloride (0·45 gram) was decomposed by hydrogen sulphide as in the preceding experiment. The filtrate was concentrated in a vacuum to 6 c.c., diluted with 4 c.c. of water, and to the resulting solution (10 c.c.) were added 10 c.c. of an aqueous solution of chloroauric acid. The solution became turbid and fine, golden-yellow needles were rapidly deposited. The yield of the gold salt, which melted and decomposed slightly at 180—184° (uncorr.), was 0·465 gram. It was found to contain no water of crystallisation. It was freely soluble in absolute alcohol, more soluble indeed in this solvent than in water, and could be recrystallised from either solvent. On boiling the aqueous solution, some decomposition was noted.

The best way to recrystallise this salt is to dissolve it in excess of water at 40° and to concentrate the solution at a low temperature in a vacuum until crystallisation occurs. Recrystallised from water in this way, the gold compound separates as glistening, golden platelets having the same melting point and composition as the needles described above. If heated at 110—120°, the salt slowly loses weight and discolours, obviously suffering slight decomposition.

For analysis, the gold salt was heated in a water-oven at 95° until the weight was constant. Only a minute change in weight of the air-dried material occurred (Found: Au=46·9. $C_7H_{18}O_2N_2Cl_8Au_2$ requires Au=46·9 per cent.).

Glycylcholine chloride hydrochloride forms a *double salt* with mercuric chloride, which crystallises in fine, woolly needles melting at 150—156° (uncorr.). This was prepared by dissolving the hydrochloride obtained from 0·6 gram of the platinichloride in 5 c.c. of water and adding 10 c.c. of a saturated alcohol solution of mercuric chloride. It slowly loses weight on heating at 95°, as does the corresponding salt of choline, owing to the volatility of the mercuric chloride.

Preparation of Crystalline Choline.

Choline chloride (2·5 grams) was dissolved in water and the chlorine removed from the solution by shaking with freshly-precipitated silver oxide. The silver chloride and oxide were filtered off and the solution was concentrated in a vacuum (water-bath at 30—35°). A viscous syrup was obtained, from which a small amount of silver oxide separated. The syrup was dissolved in 70 c.c. of absolute alcohol, and after the suspended silver oxide had been filtered off, the solution was again evaporated in a vacuum. The flask in which the operation was carried out was provided with a capillary bubbling-tube, to which a soda-lime tube was attached, in order to remove carbon dioxide from the air drawn through the liquid. Again a syrup was obtained. Absolute alcohol (70 c.c.) was added and the solution once more evaporated in a vacuum. The viscous syrup obtained was shaken three times with about 50 c.c. of dry ether, the bulk of the ether being removed by means of a pipette. Finally, the residual ether was removed in a vacuum (water-bath heated at 40°). The flask was then transferred to a vacuum desiccator containing phosphoric oxide. After twenty-four hours, a crystalline crust had been formed on the surface of the pasty mass. This was broken up with a glass rod and returned to the desiccator. After remaining for several days, the entire mass became crystalline. About 30 c.c. of dry ether were added and the crystalline material was ground to a coarse powder under the surface of the ether, which was afterwards removed by distillation in a vacuum.

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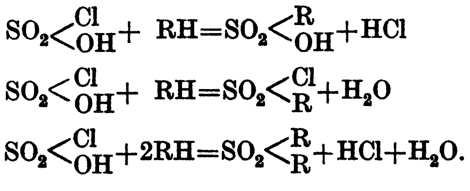
[*Received, June 21st*, 1921.]

CXLII.—*The Sulphonation of Toluene with Chlorosulphonic Acid.*

By LEONARD HARDING.

SINCE the publications of Noyes (*Amer. Chem. J.*, 1886, **8**, 176), Klason and Vallin (*Ber.*, 1879, **12**, 1851) and Monnet (Eng. Pat. 25273), the toluenesulphonyl chlorides have been prepared directly by the use of chlorosulphonic acid. Although the preparation is of technical importance, very little information is to be found on the relative proportions of the *ortho*- and *para*-isomerides obtained under varying conditions of temperature, etc. Holleman (*Ber.*, 1911, **44**, 2504) gives such details for varying conditions, using sulphuric acid, and records one result obtained with chlorosulphonic acid. It is, however, doubtful how far the results of Holleman are of use in studying the present-day direct method for the manufacture of the sulphonyl chlorides, as the mechanism of the reaction between toluene and chlorosulphonic acid has not previously been investigated.

Some earlier workers have made suggestions on the nature of the reaction, but these were usually the outcome of observations made with molecular quantities; for example, Beckurts and Otto (*Ber.*, 1878, **11**, 2061) suggest that with molecular proportions the following reactions take place simultaneously:



$$\mathrm{SO_2}{<}\substack{\mathrm{Cl}\\ \mathrm{OH}} + \mathrm{RH} = \mathrm{SO_2}{<}\substack{\mathrm{R}\\ \mathrm{OH}} + \mathrm{HCl}$$

$$\mathrm{SO_2}{<}\substack{\mathrm{Cl}\\ \mathrm{OH}} + \mathrm{RH} = \mathrm{SO_2}{<}\substack{\mathrm{Cl}\\ \mathrm{R}} + \mathrm{H_2O}$$

$$\mathrm{SO_2}{<}\substack{\mathrm{Cl}\\ \mathrm{OH}} + 2\mathrm{RH} = \mathrm{SO_2}{<}\substack{\mathrm{R}\\ \mathrm{R}} + \mathrm{HCl} + \mathrm{H_2O}.$$

Later, Houmann (*Ber.*, 1882, **15**, 1114), whilst leaving the matter an open question, suggests that the sulphonic acids are first formed and are subsequently converted into the sulphonyl chlorides by excess of acid. It has, however, been generally inferred, and the patent literature (for example, Barge, Eng. Pat. 1877, 1903) has tended to emphasise the impression, that the reaction between toluene and an excess of chlorosulphonic acid can be thus represented:

$$\mathrm{C_6H_5{\cdot}CH_3 + SO_3HCl = CH_3{\cdot}C_6H_4{\cdot}SO_2Cl + H_2O}$$
$$\mathrm{H_2O + SO_3HCl = H_2SO_4 + HCl.}$$

The following work was carried out with the object of obtaining further information on the mechanism of the reaction and details as to the maximum quantity of the *ortho*-isomeride which might be obtained by a variation of the experimental conditions.

EXPERIMENTAL.

Preparation of Materials.

The chlorosulphonic acid was prepared from commercial acid of 95 per cent. purity by distillation in a current of hydrogen chloride gas. The toluene was a well-washed commercial specimen distilling within 0·3°.

Where pure toluenesulphonic acids were required, they were prepared by hydrolysing the pure sulphonyl chlorides with water, the latter being obtained by the method described by the author (this vol., p. 260).

Method of Analysis.

The sulphonyl chlorides were obtained from the reaction product by pouring on to ice and extracting with ether in the usual way. The ethereal solution was not dried, as only comparative data were required with regard to yields.

The estimation of the proportion of the *o*- and *p*-isomerides in the mixed sulphonyl chlorides was made by converting them to the amides. Owing to the presence of by-products and impurities in the sulphonyl chlorides, it was necessary to purify the crude amides. The method adopted was to dissolve them in a slight excess of 10 per cent. sodium hydroxide and shake with a few drops of chloroform to remove small quantities of the *meta*-isomeride and an easily fusible, brown substance, which has not yet been identified. After separating and filtering the alkaline solution, the whole of the amide was precipitated with a slight excess of acid. The purified amide having been dried and the melting point taken, the composition was ascertained by reference to the melting-point curve of McKie (T., 1918, **113**, 799). The method of purification described was quite satisfactory for comparative purposes, as was proved by the fact that, when known mixtures were treated in the same way, no difference in melting point between the original mixture and the reprecipitated amides was observable. Also in the majority of operations duplicate tests were carried out and the same results obtained. In the case of all purifications, the same relative quantities of reagents and wash-water were used in order to avoid error from the difference in solubility of the *o*- and *p*-sulphonamides.

The Experiments.

(1) It was considered desirable first to ascertain the effect of sulphonating at low temperatures. On making the preliminary experiment of adding toluene to chlorosulphonic acid which had previously been cooled with solid carbon dioxide to —40°, no visible signs of reaction could be observed. In order to ascertain whether any reaction would take place after long contact with the acid at the temperature of solid carbon dioxide, 10 grams of toluene were mixed with 40 grams of chlorosulphonic acid which had been cooled to below —40°. The tube containing the mixture was placed in a vacuum vessel, closely packed with solid carbon dioxide, and the whole placed in the refrigerator overnight. After eighteen hours, the mixture was poured on to ice, 6·9 grams of toluene were decanted off the ice-water, and although there was a slight coloration, no trace of sulphonyl chloride could be detected in the residue after evaporation of the toluene. By treating the water in the usual manner 1·3 grams of sodium toluenesulphonate were obtained, which, on treatment with phosphorus pentachloride and subsequent amidation of the sulphonyl chlorides produced, gave a mixed amide containing 58·5 per cent. of the *para*-isomeride.

(2) A similar experiment was made and an amide obtained containing 59·5 per cent. of the *para*-isomeride.

(3) Ten grams of toluene were gradually added during several hours to 40 grams of chlorosulphonic acid, each small addition being made after cooling the acid to —40° and then allowing the mixture to warm up in the air to —35°. When the whole of the toluene had been added and the mixture had remained below —35° for about three hours, the whole was poured on to ice. All the toluene had reacted, but only 4·3 grams of mixed sulphonyl chlorides were obtained, the composition corresponding with 53·5 per cent. of the *para*-isomeride.

(4) Two separate mixtures of toluene and chlorosulphonic acid having been made at a temperature below —40° in the same proportions as before, they were poured gradually into tubes surrounded by ice and the reaction was allowed to take place at 5—10°. One of the mixtures was poured on to ice immediately and the other after remaining for two hours. The sulphonyl chlorides obtained (16·9 grams) had in each case a composition corresponding with 52·5 per cent. of the *para*-isomeride.

In the following determinations the toluene (10 grams) was added in fine droplets to the cooled and vigorously stirred acid.

Expt.	Proportion of toluene to acid.	Temperature.	Yield of undried sulphonyl chlorides. Grams.	Percentage of *para*-isomeride.
5	1 : 4	−15°	7·9	57·5
6	,,	,,	7·0	,,
7	,, (acid not distilled)	5—10	17·7	73
8	,, (acid distilled)	,,	19·3	,,
9	1 : 8	,,	21·6	,,
10	1 : 4	20—25	—	76·5
11	,,	35—40	—	86·0
12	,,	75—80	—	94·5

(13) An operation similar to No. 8 was carried out except that the method of mixing the reagents was reversed, that is, the acid was added to the cooled toluene. Two different determinations gave sulphonyl chlorides having the same composition, namely, 91 per cent. of the *para*-isomeride.

From observation of the results obtained at temperatures below 0° it appeared from the unusually low yields of sulphonyl chlorides that the acids were produced before the sulphonyl chlorides, and that if molecular quantities could be made to react without the influence of any local or temporary excess of acid, no sulphonyl chlorides would result. With the object of attaining these conditions as nearly as possible, the following determinations were made.

(14) Ten grams of toluene were mixed with 12·6 grams (1 mol.) of chloro-sulphonic acid at a temperature below −40 and the mixture was poured on to the bottom of a large beaker at room temperature. The product was then poured on to ice. There resulted 2 grams of sulphonyl chlorides, together with 0·76 gram of a white solid suspended in the acid water, which was not soluble in ether. The solid crystallised from chloroform in monoclinic prisms, melted at 158°, and was evidently di *p*-tolylsulphone. The ice-water was treated in the usual manner and 9·38 grams of sodium toluenesulphonate were obtained, which on subsequent treatment showed a composition corresponding with 80 per cent. of the *para*-isomeride.

(15) Another attempt to avoid, if possible, the influence of excess of acid was made by carrying out the reaction in excess of toluene. The chlorosulphonic acid (126· grams) was gradually added with vigorous stirring to 10 grams of toluene whilst the temperature was maintained at 5—10°. One gram of sulphonyl chlorides resulted, together with 0·86 gram of sulphone, and 5·43 grams of sodium toluenesulphonate were obtained by treatment of the ice-water. The sodium salt on further treatment showed a composition indicating 80 per cent. of the *para*-isomeride.

In interpreting the above experimental results it is to be noted that, when the temperature is sufficiently low, no sulphonyl chlorides are produced, although a large excess of chlorosulphonic acid is present. Even when the temperature is raised to −35°, only a low yield is obtained. But if similar mixtures are allowed to rise in temperature to 0° (Expt. 4), the sulphonyl chlorides are mainly produced. When these considerations are coupled with the fact that when 1 molecule only of chlorosulphonic acid is employed (Expt. 15) the main product is the acid, whereas when an excess of acid is finally added (Expt. 13) the sulphonyl chlorides are the main product, it appears clear that the action of an excess of chlorosulphonic acid on toluene must be represented by the following equations:

$$C_6H_5\cdot CH_3+SO_3HCl=CH_3\cdot C_6H_4\cdot SO_3H+HCl$$
$$CH_3\cdot C_6H_4\cdot SO_3H+SO_3HCl=CH_3\cdot C_6H_4\cdot SO_2Cl+H_2SO_4.$$

Assuming that the above correctly represents the reaction, it is probable that in an ordinary sulphonation the conversion from the acids to the acid chlorides will be increasingly retarded by the dilution of the remaining chlorosulphonic acid with the products of reaction. Consequently, in an industrial operation it is essential to the obtaining of good yields of sulphonyl chlorides that the mixture should be allowed to remain a sufficient length of time for the completion of the process before the products are separated. Especially is this important in view of the fact that an investigation at present in progress tends to show that the isomeric acids are not proportionately converted into the acid chlorides in dilute solutions of chlorosulphonic acid, but that the predominating acid is more quickly transformed. This may account for the fact that the proportion of *p*-sulphonyl chloride in Experiment 13 is greater than that of the *p*-sulphonic acid in Experiment 15, two similar operations, except that in the former an excess of acid has been added.

The question arose as to the possibility of intramolecular change occurring during the second stage of the reaction. Apparently no such change takes place, for when pure acids were treated at room temperature with an excess of chlorosulphonic acid the sulphonyl chlorides obtained were pure products.

Holleman (*loc. cit.*) showed in the case of sulphuric acid that the proportion in which isomerides are obtained is greatly affected by the temperature and the quantity of acid used. The same effect is to be observed, but more markedly, in the case of chlorosulphonic acid. The necessity for working with a constant excess of acid if the *ortho*-isomeride is required is emphasised still more by reversing the usual method of sulphonation, as in Experiment 13, where the reaction took place in excess of toluene and the result was a largely increased amount of the *para*-isomeride.

It will therefore be evident that any local excess of toluene should be avoided if the *ortho*-isomeride is required in maximum yield. This idea has already been abroad in industry and, in consequence, some workers spray the toluene into the acid in order to prevent local excess of the former as far as possible. The question has arisen as to how far the subdivision of the toluene increased the proportion of the *ortho*-isomeride. In Experiment 4, where the whole of the toluene has been previously dissolved in the chlorosulphonic acid at a low temperature, we have the effect of infinite subdivision, and one can therefore assume that the result is indicative of the maximum proportion of the *ortho*-isomeride obtainable by any ordinary method of sulphonation at that temperature.

Considering the influence of temperature, it might have been expected that the acids produced in Experiment 1 would have contained the greatest proportion of the *ortho*-isomeride, but it appears that there is an early limit to the effect of temperature in this direction. It is not clear at the moment why the proportion of the *ortho*-isomeride should be greatest in Experiment 4, but it is hoped that further investigation of this most susceptible reaction will lead to an explanation of this and other difficulties.

I should like to take this opportunity of thanking Professor Sir W. J. Pope for his helpful advice and interest in the work.

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CXLIII.—*Studies on Hypophosphorous Acid. Part III. Its Reaction with Mercuric Chloride.*

By ALEC DUNCAN MITCHELL.

THE reaction between hypophosphorous acid and iodine has been studied by Steele (T., 1907, **91**, 1641) and submitted to a more detailed examination by the author (T., 1920, **117**, 1322), who had resorted to it in the hope of throwing more light on the reaction now discussed. It had been found that the reactions were exactly comparable when the solutions were not too dilute. As the elucidation of the problem was found to depend on the reaction velocities at very low concentrations of iodine and mercuric chloride respectively, the former reaction was the more suitable for study because the small concentrations of iodine could be accurately determined, whereas, in the method originally adopted for following the reaction in the case of mercuric chloride (series A), the small concentrations were found by difference and were very susceptible to error. A further method has now been utilised, which, to some extent, overcomes this difficulty (series B).

In the communication mentioned, the hypothesis suggested as agreeing with the observed facts was as follows. Hypophosphorous acid *molecules* are in equilibrium with a very small proportion of an active form called, for convenience, H_5PO_3; this reacts very rapidly with the tri-iodide ion :

$$H_5PO_3 + I'_3 = H_3PO_3 + 2H^{\cdot} + 3I',$$

and the equilibrium thus displaced is restored at a finite rate which is accelerated by hydrogen ions : $H_3PO_2 \longrightarrow H_5PO_3$. The latter constitutes the measurable reaction unless the iodine (or mercuric chloride) is very dilute.

The mathematical development of this hypothesis led to the expression

$$(1 + rh_t/a_t)ds/dt = kl_t(1 - \alpha_t)h_t,$$

where l_t, h_t, and a_t were the concentrations of hypophosphorous acid, hydrogen ions, and iodine molecules respectively at time t, ds/dt was the rate of formation of phosphorous acid, and α_t the degree of ionisation of hypophosphorous acid at that time; r and k were constants. This expression was obtained by making several simplifying approximations, but was shown to hold with fair accuracy for all experiments under varying conditions. The fact that r is small accounted for the very slight effect of the iodine concentration on the velocity until that concentration became very small; k is the constant of the direct reaction involved in the equilibrium : $H_3PO_2 \rightleftharpoons H_5PO_3$ (p. 1275).

The reaction with mercuric chloride shows the same characteristics as that with iodine. Moreover, the measurable velocity under similar conditions is almost the same in the two cases, provided that the concentration of the iodine or mercuric chloride does not fall below about one-fiftieth or one-twentieth molar respectively, so that it is still more probable that neither takes any part in the predominating reaction (see Table IV).

The hypothesis can now be adapted for consideration of the present reaction. The equilibrium reaction is the same as before, but when one considers the rapid reaction in which the mercuric chloride takes part, a modification is necessary. The mercuric chloride may function as (1) molecules, (2) the $HgCl^{\cdot}$ or $Hg^{\cdot\cdot}$ ions, or (3) $HHgCl_3$ or a similar complex or corresponding ions (see Linhart, *Amer. J. Sci.*, 1913, [iv], **35**, 353). It is only very slightly ionised in its pure solutions, but in the presence of hydrochloric acid there is a marked tendency to form the complex ion $HgCl'_3$ (Sand, *Zeitsch. physikal. Chem.*, 1907, **59**, 424). In its general form the expression given above becomes

$$[1+rh_t/f(a_t,h_t,c_t)]ds/dt=kl_t(1-\alpha_t)h_t,$$

c_t being the corresponding concentration of chloride ions, and the function can be given precise mathematical expression according to the part played by mercuric chloride in the rapid reaction. As the term involving this function only becomes appreciable at very low concentrations of mercuric chloride, where the experimental error in determining both ds/dt and a_t is proportionately large, it was decided to use a method whereby unchanged mercuric salt could be estimated directly (series B). The fairly consistent results obtained when the concentration of mercuric chloride does not fall below 0·05 molar (as in series A) show that the omission of this term causes no serious error in such cases, for which, therefore, the expression $ds/dt=kl_t(1-a_t)h_t$ is used; h_t is found to be a linear function of s and is put equal to $h+ms$, m being a constant for each particular experiment; l_t is equal to $l-s$; as α_t is not always a linear function of s, the expression is integrated assuming $(1-\alpha_t)$ to be constant, and, in calculating the value of k for any particular period, the value of $(1-\alpha)$ at the middle of that period, $(1-\alpha_{H})$, is used for $(1-\alpha_t)$. The integrated form is:

$$(h+ml)(1-\alpha_{H})kt=\log_e l/l_t+\log_e h/h_t \quad . \quad . \quad (1)$$

letters without suffixes denoting initial values.

The mean value of the constant obtained, 134×10^{-5} (see Tables I and II), agrees with that obtained in the iodine series, 128×10^{-5}, but in both cases the highest results were obtained with the highest concentrations of hypophosphorous acid, thus indicating a slight secondary disturbing effect.

In series B, lower concentrations of mercuric chloride were used and the mercury in solution was determined directly. The "constants" calculated on formula (1) show a definite diminution with decreasing concentrations of mercuric chloride and hypophosphorous acid. A few experiments were carried out in presence of $N/2$- or $N/10$-sodium chloride, and these gave a distinctly lower constant than the corresponding experiments without sodium chloride, after allowance had been made for the consequent decrease in the hydrogen ions derived from the hydrochloric acid. This points to a marked decrease in the second (rapid) reaction and must be due to the formation of complexes at the expense of undissociated mercuric chloride or its ions; the complex is therefore not the active form of mercuric chloride, as was anticipated from analogy with the complex iodide (p. 1271), although Linhart (*loc. cit.*) finds that, in the reaction between phosphorous acid and mercuric chloride, it is the complex which reacts.

Constants for the various equilibria involved are available. Morse (*Zeitsch. physikal. Chem.*, 1902, **41**, 709) gives $[Hg^{\cdot\cdot}][Cl'] = 3{\cdot}5 \times 10^{-8}[HgCl^{\cdot}]$ and $[HgCl^{\cdot}][Cl'] = 28 \times 10^{-8}[HgCl_2]$, whilst Sand (*loc. cit.*), correcting the interpretation of Sherrill's results (*Zeitsch. physikal. Chem.*, 1903, **43**, 705), gives $[HgCl'_3] = 11{\cdot}5 \times [HgCl_2][Cl']$. Also Leblanc and Nóyes (*Zeitsch. physikal. Chem.*, 1890, **6**, 329) showed that the formation of complexes with mercuric chloride did not affect the ionisation of hydrochloric acid; the complex $HHgCl_3$ is therefore as strongly ionised as hydrochloric acid.

This made it possible to calculate the concentrations of the various mercury compounds, and, as ds/dt and the mean concentrations of hydrogen ions, chloride ions, $H_2PO'_2$ ions, and hypophosphorous acid molecules are readily obtained for each interval, a search was made for a rapid reaction which would satisfactorily account for the falling-off of the "constant."

In the iodine series (Mitchell, *loc. cit.*), the very small concentration of the hypothetical H_5PO_3 at time t was denoted by y_t, and it was shown that this was being continually decreased owing to the reaction with iodine, and continually increased owing to re-establishment of the equilibrium $H_3PO_2 + H_2O \rightleftharpoons H_5PO_3$: whence

$$dy/dt = kl_t h_t(1-\alpha_t) - k_1 h_t y_t - ds/dt \quad . \quad . \quad (2)$$

If now this hypothetical compound reacts with mercuric chloride as molecules, one has $2HgCl_2 + H_5PO_3 = Hg_2Cl_2 + H_3PO_3 + 2HCl$ or

$$ds/dt = k_2 y_t a^2_t \quad . \quad . \quad . \quad . \quad (3)$$

a_t being the active mass of the mercuric chloride: on elimination of y_t, and with certain approximations as before, one finds

$$[1 + rh_t/a^2_t]ds/dt = kl_t(1-\alpha_t)h_t,$$

r being a constant. The application of this formula failed to give consistent results with mercury in any form, and also failed if the reaction was supposed to be unimolecular with regard to mercury compounds, or if the hydrogen ions were assumed to catalyse the second reaction also.

The slight dependence of the "constant" on the concentration of hypophosphorous acid (which was much more marked than in the iodine series) pointed to the possibility of this, or its active form, being bimolecular in the second reaction, and, after examining several possible reactions, it was found that the only one to give any approach to consistent results, both in individual experiments and in all, was that involving one molecule of mercuric chloride as such and two molecules of hypophosphorous acid, which suggests the formation and rapid decomposition of an intermediate compound. This requires that

$$ds/dt = k_2 y^2_t a_t \quad . \quad . \quad . \quad . \quad (4)$$

in place of (3). Elimination of y_t between (4) and (2) produces a very complicated expression. After neglecting differentials of the second order and second degree (which have small coefficients and are of opposite sign), one obtains

$$(ds/dt)/h_t l'_t + (r/l'_t)\sqrt{(ds/dt)/a_t} = k' \quad . \quad . \quad (5)$$

or

$$v + r\sqrt{h_t v/a_t l'_t} = k' \quad . \quad . \quad . \quad . \quad (6)$$

where $l'_t = l_t(1-\alpha_t)$ and $v = (ds/dt)/h_t l'_t$, r being, as before, a constant. This is also obtained more directly if one assumes that $dy/dt = 0$, which is justified because y_t is very small and its differential is of a lower order of magnitude than ds/dt and the other terms in (2). This expression cannot be integrated, since a_t is a complex function of A_t, the total mercuric chloride, and therefore of s; but when r is put equal to 0·0014, it gives fairly concordant values for the intervals in each experiment, in spite of the fact that the error in determining ds/dt is considerable when a is small. This correction term is applied to the experiments in series B, and the mean constants thus obtained (as in Experiment XXVI, which is given as an example) are shown in Table III, where $v' = r\sqrt{h_t v/a_t l'_t}$, $k' = v + v'$, and n represents the amount of mercuric chloride existing as the complex ion $HgCl'_3$ and not reacting, so that $a_t = A_t - n_t$.

EXPERIMENTAL.

The course of the reaction in series A was followed by alkali titrations. Since hypophosphorous acid behaves as a monobasic acid with either methyl-orange or phenolphthalein as indicator, whereas both phosphorous and phosphoric acids are monobasic with regard to methyl-orange and dibasic with regard to phenolphthalein, it was expected that the use of these two indicators would accurately show the course of the reaction. With certain precautions this expectation proved to be correct.

In following the reactions:

$$\text{(I)}\ H_3PO_2 + 2HgCl_2 + H_2O = H_3PO_3 + Hg_2Cl_2 + 2HCl$$

and

$$\text{(II)}\ H_3PO_2 + 4HgCl_2 + 2H_2O = H_3PO_4 + 2Hg_2Cl_2 + 4HCl,$$

if l is the original titre of the hypophosphorous acid with regard to both indicators, after an amount s has been oxidised, one would have titres as follows: for reaction (I) only, $l+2s$ (methyl-orange) and $l+3s$ (phenolphthalein); for reaction (II), $l+4s$ (methyl-orange) and $l+5s$ (phenolphthalein). In all the experiments the increase in the methyl-orange titre was, within the limits of experimental error, equal to two-thirds of the increase in the phenolphthalein titre up to the point where reaction (I) was complete; a very slow subsequent change in the sense of reaction (II) was then just perceptible. The oxidation to phosphoric acid was therefore negligible under the conditions of experiment.

An acid solution of mercuric chloride may be titrated by sodium hydroxide, using methyl-orange as an indicator, without the formation of a precipitate, but before the hydrogen-ion concentration is reduced to that corresponding to an end-point with phenolphthalein, a precipitate is formed. In titrating the reaction liquid the presence of the precipitated mercurous chloride did not obscure the end-point with methyl-orange, but when this had been determined an excess of strong potassium iodide solution was added and the resulting mercury was rapidly deposited as a grey powder, leaving a clear pale yellow liquid in which the end-point with phenolphthalein could easily be seen. The addition of the potassium iodide stopped the reaction completely, and blank experiments showed that it did not affect the result in any way; owing to the pale yellow colour produced, the potassium iodide could not be used to stop the reaction in the first place, before the titration with methyl-orange, but the neutralisation of the hydrogen ions effected this sufficiently quickly.

Various test experiments led to the following conclusions. (*a*) The accuracy of the indicator scheme outlined was tested on solutions of the three acids separately. (*b*) The possibility of alternate formation and reduction of phosphoric acid was excluded by a trial on mixed solutions of hypophosphorous and phosphoric acids which did not vary in titre (using phenolphthalein) over a period of several days: any interaction would have increased this titre owing to the production of phosphorous acid at the expense of hypophosphorous acid. (*c*) In solutions neutral to methyl-orange the reaction was negligibly slow. (*d*) Reaction ceases completely when excess of potassium iodide is added, the resulting complex ion, HgI''_4, not being reduced perceptibly by hypophosphorous acid under the experimental conditions over a period of several weeks. (*e*) Under comparable conditions, phosphorous acid reduces mercuric chloride at less than one-thousandth of the rate of reduction by hypophosphorous acid. (*f*) Mercurous chloride is not perceptibly reduced to metallic mercury under the experimental conditions.

The stock solution of hypophosphorous acid was the same specimen as that used in the iodine series (*loc. cit.*). It was chemically pure except for a small percentage of phosphorous acid, and, from analytical data (both volumetric and gravimetric) given previously, was found to be 5·25 molar with respect to the former and 0·20 molar with regard to the latter. The presence of this phosphorous acid is allowed for both in the titrations and in the calculations of the hydrogen-ion concentrations.

In series B a direct method of estimation of mercuric chloride was used. None of the standard volumetric methods for the estimation of mercuric salts is suitable for use in the presence of mercurous salts. For this reason the reaction mixture was run into a slight deficiency of *N*/2-sodium hydroxide solution; the reaction was thereby nearly stopped, and 2 grams of sodium chloride were added, which served both to prevent an apparent "lag" in the precipitation of mercurous chloride, noticed by Montemartini and Egidi (*Gazzetta*, 1902, **32**, ii, 182), and also to inhibit to a sufficient extent a secondary reaction between alkali and mercuric chloride at the neutral point in titrations. The mercurous chloride was rapidly filtered and washed in a Gooch crucible, using a small circle of filter-paper instead of asbestos.

Many of the published methods for the volumetric estimation of mercuric chloride were investigated, but few were found to be sufficiently accurate except under very restricted conditions as to concentration, neutrality, and presence of alkaline chlorides. The method ultimately adopted depends on the fact, first utilised by Rupp (*Chem. Zeit.*, 1908, **32**, 1077), that potassium cyanide, when added to neutral solutions of mercuric chloride, produces un-ionised mercuric cyanide, and the excess of the potassium cyanide can be accurately titrated with hydrochloric acid. It was feared that in very dilute solutions this method might fail to give good results owing to possible slight ionisation of the mercuric cyanide, but test estimations on 0·20 to 0·50 c.c. of *M*/5-mercuric chloride in 50 to 100 c.c. of water showed that the method was still accurate.

The filtrate is exactly neutralised by sodium hydroxide using bromophenol-blue (tetrabromophenolsulphonephthalein) as indicator; a slight excess of *N*/10-potassium cyanide is then added, as shown by a pronounced deepening of the colour of the indicator, and this excess is titrated by *N*/10-hydrochloric acid to the same tint of indicator as obtained before the addition of the potassium cyanide. The direct titration with potassium cyanide using phenolphthalein as indicator, as suggested by Rupp, was found not to give such good results. The use of methyl-orange gives similar results, but bromophenol-blue was preferred because it has almost the same effective range as methyl-orange and was found to be more suitable for use in artificial light. Methyl-red was not so effective, as it is more sensitive to carbon dioxide and gives indefinite results in presence of phosphorous acid. Blank estimations showed that neither hypophosphorous nor phosphorous acid affected the result.

The methods described agree closely, and almost identical results were obtained for experiments VII and XXI, which are done by the different methods but are otherwise comparable.

The reactions were carried out in stoppered, brown glass bottles in a thermostat at 25±0·05°. The requisite volumes of *M*/5- or *M*/10-mercuric chloride solution and standardised hydrochloric acid solution (when used) were made up to 400 c.c. or 1000 c.c., and 1·013, 2·000, or 4·000 c.c. of stock hypophosphorous acid solution were added from standardised pipettes when the liquids had attained the temperature of the thermostat. From time to time definite volumes were withdrawn by a pipette, allowed to run into an equal volume of cold water, and treated as described in series A or B.

In the tables given, all concentrations are multiplied by 200 in order to avoid small decimals and the constants are in the same units. At the head of the tables are shown, $A-2s$, the total mercuric chloride concentration in moles per 200 litres; a, the mercuric chloride which is not present as a complex; t, the time in minutes; s, the amount of hypophosphorous acid oxidised; $l-s$, the amount remaining; HCl, the total hydrochloric acid; $H^{\cdot}_{HCl}$, the hydrogen ions derived therefrom, the degree of ionisation being taken from the data of Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781); α, the degree of ionisation of the hypophosphorous and phosphorous acids, obtained by the graphical methods described by the author in the case of the iodine series (*loc. cit.*); $H^{\cdot}_{\rho}$, the hydrogen ions derived from these two acids, which is equal to $l\alpha$; h, the total of the hydrogen ions; and $(1-\alpha_H)$ the value of $(1-\alpha)$ half-way through the period for which the constant, k, is calculated. The value of m, the coefficient of the change in h, is also given (see p. 1268).

In those experiments in which sodium chloride is used, the concentration of hydrogen ions is obtained by graphical methods similar to those used in the case of hypophosphorous and hydrochloric acids, but modified to allow for the fact that in the latter case no allowance was made for the effect of the hypophosphorous acid on the hydrochloric acid, whereas in the case of sodium chloride and hydrochloric acid there is a mutual influence. These methods are based on the "total ion" hypothesis that "the degree of ionisation of each salt in a mixture is the same as in a solution of the pure salt at the same total ion concentration" (Bray and Hunt, *loc. cit.*), and the data utilised are those of these authors which, when extrapolated as required, agree well with those of Kohlrausch and Ostwald.

Temperature Coefficient.—An experiment (number XXXIII) was carried out at 15°. The constant obtained was $39·3 \times 10^{-5}$, and, as this experiment was otherwise identical with experiment XXII, which gave a constant of 128×10^{-5}, the temperature coefficient for ten degrees is 3·26, whereas the value obtained in the case of the iodine series was 3·14.

SERIES A.

The following twelve experiments were without initial hydrochloric acid. Experiment II is given in detail and the others are summarised in Table I.

EXPERIMENT II.

($A = 36·7$; $m = 1·549$.)

t.	$2s$.	$l - s$.	$H^{\cdot}_{HCl}$.	α.	$H^{\cdot}_{p}$.	h.	$1 - \alpha_H$.	$k \times 10^5$.	$2s'$.
0	—	20·60	—	0·553	11·83	11·83	—	—	—
5	1·72	19·74	1·67	0·535	11·45	13·12	0·456	146	1·77
15	5·81	17·70	5·52	0·495	10·60	16·12	0·476	148	5·78
25	10·78	15·29	10·15	0·461	9·89	20·04	0·495	148	10·78
35	16·26	12·47	15·12	0·427	9·13	24·25	0·513	155	16·31
50	24·49	8·35	22·41	0·388	8·31	30·72	0·539	157	24·54
60	29·15	6·03	26·53	0·367	7·85	34·38	0·556	157	29·16
70	32·80	4·20	29·65	0·353	7·58	37·23	0·573	155	33·00
80	35·05	3·08	31·55	0·344	7·36	38·91	0·586	150	35·05
95	36·55	2·33	32·90	0·338	7·24	40·14	0·606	(135)	36·59
							Mean	152	

$2s$, in this and all other experiments, is obtained from two-thirds of the increase in the phenolphthalein titre; $2s'$ is similarly obtained from the increase in the methyl-orange titre. The close agreement shows that the formation of phosphoric acid is negligible (see p. 1271).

Certain experiments (chiefly duplicates) were done only in the initial stages, which were required for the early part of this work. As these involved only two or three readings they are only given half-weight in determining the mean and are indicated by an asterisk.

TABLE I.

Expt.	A.	l.	a.	$H^{\cdot}_{\rho}=h_0$.	m.	$k\times10^5$.	$\delta\times10^5$.
*IIA	36·7	20·6	0·553	11·83	(1·549)	137	–
*IIB	36·7	20·6	0·553	11·83	(1·549)	146	–
IIC	36·7	20·6	0·553	11·83	1·543	152	1
III	37·1	10·4	0·645	6·98	1·609	130	6
IIIA	37·1	10·4	0·645	6·98	(1·609)	130	2
VII	19·1	10·5	0·645	6·98	1·607	130	3
*VIIA	19·1	10·5	0·645	6·98	(1·607)	129	–
VIII	19·0	20·6	0·553	11·83	1·528	141	5
*VIIIA	19·0	20·6	0·553	11·83	(1·528)	148	–
VIIIB	19·0	20·6	0·553	11·83	(1·528)	144	3
X	38·3	5·3	0·735	4·05	1·657	129	9

The column δ shows the maximum deviation from the mean in each case.

The following seven experiments were with initial hydrochloric acid. Experiment IX is given in detail and the others in summary —Table II.

EXPERIMENT IX.

(A=19·08; m=1·645.)

t.	$2s$.	$l-s$.	HCl.	$H^{\cdot}_{HCl}$.	a.	$H^{\cdot}_{\rho}$.	h.	$1-a_H$.	$k\times10^5$.
0	—	10·40	11·20	10·50	0·495	5·34	15·84	—	—
5	0·95	9·93	12·15	11·36	0·485	5·24	16·60	0·510	(112)
20	4·23	8·29	15·43	14·35	0·463	5·00	19·35	0·521	125
30	6·54	7·13	17·74	16·41	0·447	4·83	21·24	0·529	128
45	10·00	5·40	21·20	19·50	0·425	4·59	24·09	0·540	134
60	12·46	4·17	23·66	21·65	0·412	4·45	26·10	0·553	132
75	14·98	2·91	26·18	23·98	0·400	4·32	28·30	0·564	132
90	16·84	1·98	28·04	25·52	0·390	4·22	29·74	0·575	134
120	18·45	1·17	29·65	26·89	0·383	4·13	31·02	0·588	123
								Mean	130

TABLE II.

Expt.	A.	l.	HCl.	$H^{\cdot}_{HCl}$.	a.	$H^{\cdot}_{\rho}$.	h.	m.	$k\times10^5$.
VI	37·8	10·30	11·10	10·41	0·500	5·35	15·76	1·643	135
XI	38·0	10·30	5·77	5·48	0·555	5·94	11·42	1·639	134
*XVI	36·2	10·04	9·44	8·88	0·513	5·36	14·24	1·667	116
*XVII	18·1	10·04	9·44	8·88	0·513	5·36	14·24	1·647	119
*XVIII	36·2	10·04	4·72	4·50	0·572	5·97	10·47	1·604	120
*XIX	18·1	10·04	4·72	4·50	0·572	5·97	10·47	1·625	114

Mean value of k for all experiments in series A, allowing only half-weight to those marked * $=134\times10^{-5}$.

SERIES B.

Experiment XXVI is here given in detail, first according to formula (1), and then according to formula (6).

EXPERIMENT XXVI.

(A=2·480; *m*=1·76.)

t.	2*s*.	*l*−*s*.	HCl.	$H^{\cdot}_{HCl}$.	*a*.	$H^{\cdot}_{p}$.	*h*.	$1-a_H$.	$k\times10^5$.
0	—	2·606	2·342	2·27	0·725	1·89	4·16	—	—
62	0·400	2·406	2·742	2·65	0·715	1·87	4·52	0·280	106
125	0·788	2·212	3·130	3·01	0·706	1·84	4·85	0·285	101
200	1·278	1·967	3·62	3·48	0·693	1·81	5·29	0·291	102
280	1·832	1·690	4·17	4·00	0·680	1·78	5·78	0·298	104
330	2·140	1·536	4·48	4·28	0·670	1·75	6·03	0·302	103
370	2·350	1·431	4·69	4·48	0·665	1·74	6·22	0·305	101
402	2·468	1·372	4·81	4·59	0·663	1·74	6·33	0·307	98
								Mean	102

t.	A−2*s*.	*c*.	*c*−*n*.	*n*.	*a*.	*l*′.	$v\times10^5$.	$v'\times10^5$.	$k'\times10^5$.
0	2·480	2·28	2·02	0·26	2·22	0·716			
							106	8	113
62	2·080	2·66	2·40	0·26	1·82	0·686			
							100	9	109
125	1·692	3·02	2·78	0·24	1·46	0·650			
							103	12	115
200	1·202	3·48	3·28	0·20	1·00	0·604			
							110	17	127
280	0·648	4·00	3·88	0·12	0·53	0·540			
							100	24	124
330	0·340	4·28	4·22	0·06	0·28	0·506			
							88	34	122
370	0·130	4·48	4·46	0·02	0·11	0·480			
							62	55	117
402	0·012	4·60	4·60	0·00	0·01	0·462			
								Mean	118

As *k* is based on the small difference for the interval concerned, the divergences are naturally considerable, but would be much smaller if an integrated expression could be used, as is seen by comparing the variations in *v* with those of its integrated equivalent *k* in the preceding table. The average values of *h*, *l*′, and *a* during the intervals concerned are used in calculating *v* and *v*′.

TABLE III.

Expt.	A.	HCl.	*l*.	1−*a*.	*l*′.	*h*.	*c*.	*c*−*n*.	*n*.	*a*.	$k\times10^5$.	$k'\times10^5$.
XXI	19·80	—	10·45	0·350	3·66	7·07	—	—	—	19·80	132	140
XXII	9·88	—	10·40	0·350	3·64	7·02	—	—	—	9·88	128	123
XXIII	4·95	2·39	5·20	0·328	1·70	5·94	2·31	1·84	0·47	4·48	113	111
XXIV	2·49	—	5·22	0·265	1·38	3·98	—	—	—	2·49	108	?
XXV	2·49	1·17	2·61	0·239	0·62	6·28	1·15	1·01	0·14	2·35	103	110
XXVI	2·48	2·34	2·61	0·275	0·72	4·17	2·28	2·02	0·26	2·22	102	118
*XXVII	2·47	2·34	2·61	0·264	0·69	4·01	38·50	36·50	2·03	0·44	92	126
XXVIII	2·47	3·50	2·60	0·304	0·79	5·25	1·68	1·50	0·36	2·11	102	117
*XXIX	2·47	3·50	2·60	0·295	0·77	4·94	38·50	36·50	2·08	0·44	99	133
XXX	1·00	2·35	2·09	0·255	0·53	3·92	2·28	2·17	0·11	0·88	96	118
†XXXI	2·47	3·50	2·60	0·300	0·78	5·13	9·90	9·30	1·27	1·20	99	117
XXXII	1·00	4·74	1·06	0·305	0·32	5·29	4·54	4·34	0·20	0·80	93	127

* Experiments indicated thus were in presence of *N*/2-sodium chloride.

† Experiment „ „ was „ „ „ *N*/10- „ „

TABLE IV.

Showing values of 2s *for comparable solutions of mercuric chloride and iodine respectively at times* t.

EXPERIMENT VIII.

(Mercuric chloride, A=19·0; l=20·6.)

t_5.	t_{10}.	t_{15}.	t_{20}.	t_{25}.	t_{30}.	t_{35}.	t_{40}.
1·68	(3·5)	(5·5)	7·63	(10·0)	12·62	(14·8)	16·90

EXPERIMENT II.

(Iodine, a=9·8; l=20·6.)

t_5.	t_{10}.	t_{15}.	t_{20}.	t_{25}.	t_{30}.	t_{35}.	t_{40}.
1·80	3·64	5·60	7·82	10·04	12·44	14·82	17·12

Values in brackets are interpolated from a smoothed curve.

(Two molecules of mercuric chloride are equivalent to one of iodine in their action on hypophosphorous acid.)

Summary.

1. The measurable velocity of the reaction between hypophosphorous acid and mercuric chloride, if the solutions are not too dilute, is independent of the concentration of the latter, as in the analogous reaction with iodine, and is due to the re-establishment of equilibrium between hypophosphorous acid *molecules* and the hypothetical "active" form, H_5PO_3.

2. This change is catalysed by hydrogen ions, and the reaction is therefore autocatalytic.

3. This is followed by a rapid reaction which can only be detected at low concentrations. The evidence is strong, but not quite conclusive, that this reaction takes place between one molecule of mercuric chloride (and not of its ions or possible complexes) and two molecules of "active" hypophosphorous acid.

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CXLIV.—*Negative Adsorption of Alkali Haloids by Wood Charcoal.*

By Alwyn Pickles.

Adsorption of salts from their aqueous solutions by means of charcoal is readily demonstrated, and it is also known that certain haloids are negatively adsorbed, that is, water, and not the solute, is removed by charcoal.

The haloids usually adsorbed negatively are those of the alkali metals. The amount of negative adsorption depends on temperature, the kind of charcoal used, and also on the state of division of that charcoal. Coarse charcoals scarcely show the phenomenon, whilst very fine powders do so to a remarkable degree. The charcoal used in the following experiments was birch charcoal in a very fine state of division. It had been prepared during the war for use in the newer types of gas masks and was therefore of a highly specialised nature.

N/10-Solutions of the haloids were used and 5 grams of charcoal added to each 250 c.c. The flasks containing the solutions were suspended in turn in a water-bath and frequently shaken, while the temperature was gradually raised. Precautions were taken against condensation of water in the flask. As the temperature of the mixture increased, and immediately after shaking, portions were filtered off through warmed funnels, and on cooling the concentration of the haloid in the filtrate was determined by the silver nitrate–chromate method, *N*/10- and *N*/100-solutions being used. For each salt, the same mixture, charcoal–haloid, furnished a series of readings; in other words, the same carbon was in contact with the same solution throughout the experiments. The temperature of the solution and the charcoal was not raised too rapidly, a series of readings from room temperature to 100° being taken during about half an hour. The charcoal was therefore in contact with the solution for about six minutes between each reading.

The concentrations given below are expressed as the number of c.c. of *N*/10-silver nitrate required by 10 c.c. of filtrate at room temperature.

Ammonium Bromide.

Temperature ……	10°	26°	46°	64°	83°	100°
Concentration ….	10·67	10·24	10·26	10·43	10·7	11

Ammonium Chloride.

Temperature ……	10°	28°	47°	72°	100°
Concentration …	10·2	10·1	10·2	10·4	10·9

Lithium Chloride.

Temperature ……	10°	42°	62°	80°	100°
Concentration ….	10·05	10·0	9·9	9·75	9·73

Potassium Bromide.

Temperature	10°	33°	42°	69°	100°
Concentration ...	10·3	10·1	10·35	10·60	11·2

Potassium Chloride.

Temperature	10°	29°	43°	60°	80°	100°
Concentration ...	10·1	10·04	10·1	10·2	10·25	10·3

Potassium Iodide.

Temperature	10°	23°	36°	46°	71°	82°	100°
Concentration ...	10·4	10·2	10·25	10·5	10·7	11·2	11

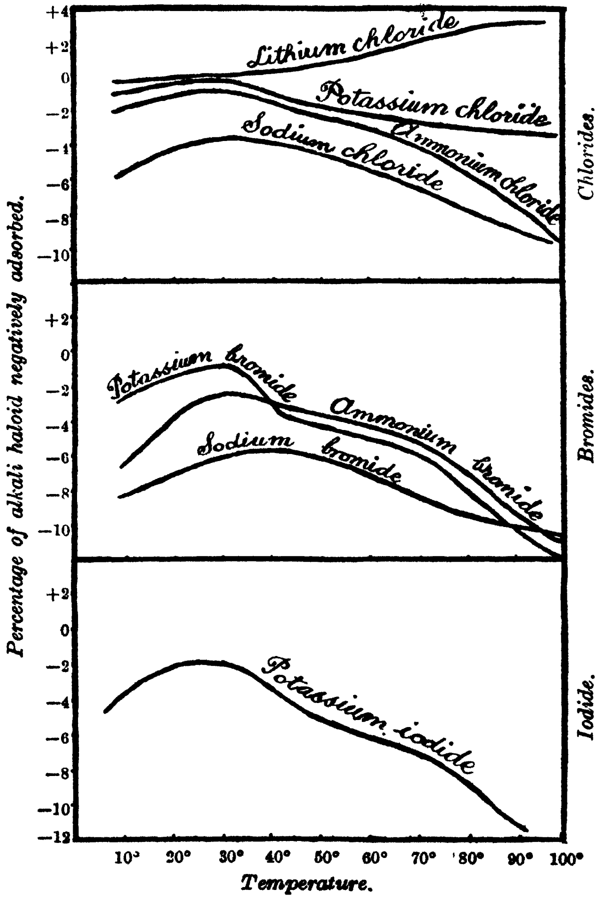
Sodium Bromide.

Temperature	12°	25°	40°	80°	100°
Concentration ...	10·82	10·7	10·58	10·88	10·97

Sodium Chloride.

Temperature	12°	25°	49°	66°	100°
Concentration ...	10·6	10·4	10·45	10·6	10·9

The results are expressed graphically in the accompanying diagram.



The decrease at the beginning is probably due to diminishing surface effect owing to the lowering of the surface tension between the liquid and the charcoal surface. As the temperature rises, however, the solvent opens up the complex interior of the charcoal by dissolving the oxidation products blocking the ends of the capillaries of the charcoal. More surface then becomes available and solute adsorption again occurs. This penetration effect with wood charcoals is often very great, as can readily be seen if experiments are made with the charcoals prepared for use in gas masks.

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CXLV.—*On the Relation between the Occlusive Power of Palladium for Hydrogen and its Activity for Catalytic Hydrogenation.*

By EDWARD BRADFORD MAXTED.

IN previous communications (T., 1919, **115**, 1050; 1920, **117**, 1280, 1501; this vol., 225), it has been shown, first, that the occlusive power of palladium for hydrogen in the presence of occluded hydrogen sulphide varies linearly with the content of inhibitant, and, secondly, that the activity of platinum for catalytic hydrogenation is also a linear function, down to a certain point of inflexion, of the content of various catalyst poisons.

If both the occlusive power and the catalytic activity are each a linear function of the same quantity, that is to say, of the content of a poison, it should follow from the laws of proportion that these two quantities, namely, the catalytic activity and the occlusive power, should also stand in a linear relationship to one another. Up to the present, however, the inhibitants and catalysts taken for occlusion measurements have not been identical with those employed for determinations of catalytic activity. In the present work, the same inhibitant, namely, lead, has been taken for each series.

EXPERIMENTAL.

For the determination of the influence of lead on the occlusion of hydrogen by palladium, the apparatus was of the same general character as that used for hydrogen sulphide (*loc. cit.*). The palladium tube was, however, provided with an attachment, by means of which regulated small volumes of dilute lead acetate solution could be admitted to the palladium without admitting air. The palladium black was prepared from the oxide by reduction in the apparatus itself, and the electrolytic hydrogen used for the measurements was purified from oxygen by passage through a tungsten filament lamp, and then treated with soda-lime and phosphoric acid, as previously described. After each addition of lead, the palladium was carefully dried, and the moisture removed from the system by evacuation.

It was found, as for hydrogen sulphide, that the influence of lead was twofold. In the first place, the occlusive power was depressed. In the second, the rate at which occlusion took place was found to be altered radically by relatively high concentrations of lead.

Table I summarises the results of a series of measurements in the presence of various proportions of inhibitant. The occlusive power refers, as before, to the volume of hydrogen absorbed at 15°, the palladium being previously evacuated at 100° by means of a mercury pump until no further evolution of gas took place. All gas volumes are reduced to 0° and 760 mm. The weight of palladium was 0·288 gram in each case.

TABLE I.

Lead content of system in milligrams.	Ratio gram-atom of Pb to 1 gram-atom of Pd.	C.c. of hydrogen occluded.	Occlusive power in c.c. of H_2 per gram of Pd.
0·0	0·0	19·7	68·5
7·3	0·013	18·2	63·2
27·0	0·048	17·1	59·4
59·5	0·105	13·9	48·3
108·0	0·193	8·3	28·8

On plotting the lead content of the system against the occlusive power, a linear relationship between these two quantities is seen to exist, analogous to that previously observed for the inhibition of the occlusive power by hydrogen sulphide. With pure palladium, and with relatively low concentrations of lead, occlusion takes place apparently instantaneously. As the content of inhibitant increases, the absorption of hydrogen becomes slower, until with a ratio of 0·19 gram-atom of lead to each gram-atom of palladium more than two weeks were required for the attainment of equilibrium. For this reason, measurements with a greater lead concentration were not carried out.

The corresponding measurements of the degree of inhibition of the catalytic activity of palladium by means of lead were carried out with the same apparatus as, and under similar conditions to, those previously used for platinum, the relative activity of the catalyst, in the presence of varied quantities of the inhibitant, being measured by the rate of hydrogenation of oleic acid in acetic acid solution at 50° and under atmospheric pressure. The lead solution employed was made by dissolving 0·0576 gram of pure lead monoxide in 50 c.c. of the purest glacial acetic acid. Part of this standard solution was still further diluted with acetic acid to one-tenth of its original strength, and thus corresponded with about 0·11 mg. of lead per c.c.

The mixture introduced into the shaking vessel for agitation with hydrogen contained in every case 3 c.c. of stock oleic acid, 0·005 gram of palladium, a varying quantity of the lead solution, and sufficient glacial acetic acid to amount, with that added with the lead, to 9 c.c. of the solvent in all.

The progress of absorption of hydrogen, in the presence of the quantities of inhibitant stated, is summarised in Table II. The volume of lead acetate solution has, for the sake of uniformity, been expressed throughout in terms of the number of c.c. of the more dilute solution (0·11 mg. of lead per c.c.), although for measurements in the presence of relatively high concentrations of lead, the stronger solution (1·1 mg. of lead per c.c.) was used.

TABLE II.

C.c. of standard lead solution added.	Lead content of system in milligrams.	C.c. of hydrogen absorbed after					
		1 min.	2 mins.	3 mins.	4 mins.	5 mins.	10 mins.
0·0	0·0	23·5	45·5	66·5	86·0	104·5	173·0
0·5	0·055	19·5	37·5	54·0	69·0	82·2	138·5
1·0	0·11	16·4	31·7	45·6	57·2	69·6	120·1
1·5	0·165	13·0	25·0	35·5	45·4	55·0	97·2
2·0	0·22	9·5	18·3	25·3	32·1	38·5	68·0
2·5	0·275	8·0	15·4	22·4	28·4	34·1	60·0
4·0	0·44	6·0	11·4	16·0	20·1	24·0	41·4
5·0	0·55	4·5	8·4	12·0	15·3	18·4	31·7
7·5	0·825	2·6	5·0	7·2	9·2	11·2	20·0
10·0	1·1	1·8	3·4	4·8	6·2	7·5	13·4
20·0	2·2	0·7	1·3	1·8	2·3	2·7	3·7

In accordance with the procedure previously adopted, the relative activity of the catalyst may be expressed by the relative initial rate of absorption of hydrogen under similar conditions. The graph representing the progress of the absorption with the time is slightly curved in form, and the initial rate is best obtained by differentiation from the equation to this curve, as was previously done. Table III shows the relationship between the lead content of the system and the catalytic activity of the palladium.

TABLE III.

Lead content of system in milligrams.	Ratio gram-atom of Pb to 1 gram-atom of Pd.	Relative catalytic activity of palladium.
0·0	0·0	25·0
0·055	0·0057	21·0
0·11	0·0113	17·5
0·165	0·0170	14·5
0·22	0·0226	10·5
		Point of inflexion
0·275	0·0283	9·5
0·44	0·0453	7·0
0·55	0·0566	5·0
0·825	0·085	2·8
1·1	0·113	2·0
2·2	0·226	0·8

If the above figures be plotted graphically, it will be seen that the relationship is linear from the point corresponding with zero concentration of the poison up to a stage in which the greater part of the activity has been suppressed. In this region, a point of inflexion occurs below which the rate of decrease of catalytic activity, caused by the further addition of lead, falls off far less steeply than for the main linear portion of the curve. This result corresponds with those obtained with platinum in the presence of various inhibitants, save that the point of inflexion is here somewhat higher on the curve than was observed in the case of platinum.

It will be noted that, although the catalytic activity, for the main portion of the curve, and the occlusive power for hydrogen, probably for the whole of the curve (compare the case of hydrogen sulphide), and certainly for the greater portion, are each a linear function of the content of an inhibitant, yet the slope of the linear graph connecting respectively the occlusive power and the catalytic activity with the content of inhibitant is not the same. It requires, for example, a ratio of 0·17 gram-atom of lead to 1 gram-atom of palladium to reduce the occlusive power to one-half of its original value, whilst, in order to reduce the catalytic activity to one-half, only about 0·02 gram-atom of lead to each gram-atom of palladium is necessary. It appears not improbable that the reason for this lies in the fact that, whilst occlusion of hydrogen is not confined to the surface only of the palladium, catalysis is mainly a surface phenomenon. This view is strengthened by the observation that the slope of the poisoning line for catalytic activity varies with the fineness of division of the catalyst, so that the same stock catalyst has to be used throughout the series of measurements, whilst the poisoning coefficient for the inhibition of the occlusive power does not vary from preparation to preparation of the same metal, at any rate in the case of palladium.

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CXLVI.—*The Action of Sodium on Phenyl Acetate.*

By WILLIAM HENRY PERKIN, JUN.

MANY years ago (T., 1880, **37**, 487), a paper on this subject was published by W. R. Hodgkinson and the author, and it was shown that among the products of this action were ethyl acetate, salicylic acid, and two crystalline substances (α-), melting at 68°,* and (β-), melting at 138°, which, on analysis, gave results agreeing with the formulæ $C_{15}H_{12}O_3$ and $C_{18}H_{14}O_4$ respectively. It was suggested that these crystalline substances were possibly produced from an acetoacetic ester—presumably phenyl acetoacetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}C_6H_5$—but the study of Organic Chemistry had, at that time, not sufficiently developed to make it possible to determine the structure of these two substances. A recent perusal of the small paper seemed to the author to indicate that the results therein described were curious and interesting enough to warrant a more complete investigation of the matter, and this has now been carried out.

A number of comparative experiments on the action of sodium on phenyl acetate have therefore been made, and these have confirmed, in the first place, the original statement that ethyl acetate and salicylic acid are among the products of the decomposition. It has furthermore been established, by conversion into the *p*-bromophenylhydrazone, that acetone is a constituent of the low-boiling fraction of the products of the interaction. The formation of *ethyl acetate* under the strongly alkaline conditions which prevail is curious, and is possibly due to the reduction of part of the phenyl acetate to alcohol which, in the form of sodium ethoxide, at the high temperature of the reaction, may act on some of the phenyl acetate thus :

$$CH_3{\cdot}CO_2{\cdot}C_6H_5+NaOEt=CH_3{\cdot}CO_2Et+NaO{\cdot}C_6H_5$$

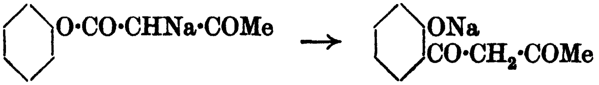
---

* The melting point given is 48°, but reference to the original notes shows that this is a misprint for 68°.

The fact that *salicylic acid*, sometimes in quite considerable quantity, is always formed during the process seems at first remarkable, but its formation may be explained by a scheme which appears to be also essential to the explanation of other changes to be discussed below. Judging from the analogy of the action of sodium on ethyl acetate, it may be assumed that the action of sodium on phenyl acetate leads to the formation of the sodium derivative of phenyl acetoacetate,

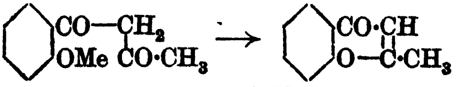
$$2CH_3\cdot CO_2\cdot C_6H_5+2Na=CH_3\cdot CO\cdot CHNa\cdot CO_2\cdot C_6H_5+NaO\cdot C_6H_5+H_2,$$

and it is unfortunate that all attempts to prepare phenyl acetoacetate have so far been unsuccessful, but experiments with this object are being continued. At the high temperature of the interaction it is not surprising that this substance does not remain, and it may well be assumed that the following intramolecular change—comparable with the formation of sodium salicylate from sodium phenylcarbonate—takes place:



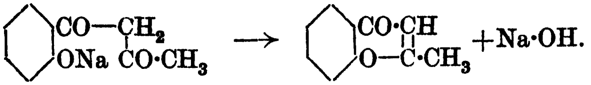
Sodium derivative of
o-hydroxybenzoylacetone (I.)

The sodium phenoxide or other alkali present in large quantity may then decompose this substance with formation of salicylic acid and acetone, and it is significant that, as mentioned above acetone was always found as a constituent of the low-boiling products of the action of sodium on phenyl acetate. There remained still the explanation of the constitution and mechanism of formation of the two crystalline substances α- (m. p. 68°) and β- (m. p. 138°) described in the earlier communication (T., 1880, **37**, 489), and this was rendered difficult by reason of the small quantities—often less than 1 per cent.—of these substances which are produced during the action of sodium on phenyl acetate. Several grams of the substance α- were, however, collected and carefully purified, when it was found that the melting point is 71°, and not 68°, and that the substance has the formula $C_{10}H_8O_2$, and not $C_{15}H_{12}O_3$, as suggested in the earlier paper. A careful investigation ultimately established the fact that it is 2-methylbenzo-γ-pyrone, identical with the substance produced when *o*-methoxybenzoylacetone is boiled with hydriodic acid (Block and Kostanecki, *Ber.*, 1900, **33**, 1999):



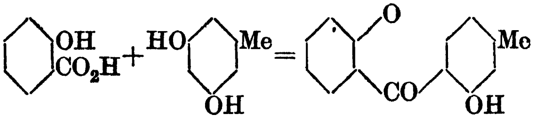
2-*Methylbenzo-γ-pyrone.*

The formation of this substance during the action of sodium on phenyl acetate may be explained by the conversion of the sodium derivative of phenyl acetoacetate into the sodium derivative of *o*-hydroxybenzoylacetone (see above) and subsequent internal condensation with elimination of sodium hydroxide :



The second crystalline substance, β-, obtained from the product of the action of sodium on phenyl acetate, was found to melt at 142°, or rather higher than previously stated (138°; *loc. cit.*, p. 489), and a close study of its properties described in the experimental section ultimately led to the discovery that it is 1-hydroxy-3-methylxanthone.

An examination of the literature showed that this substance had already been described by Michael (*Amer. Chem. J.*, 1883, **5**, 95), who obtained it by the condensation of orcinol with salicylic acid in the presence of zinc chloride :

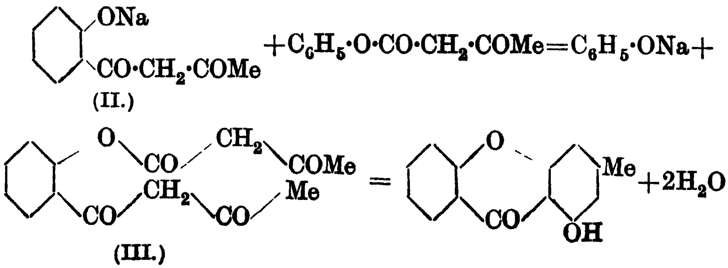


It is stated to crystallise in yellow needles and melt at 140°.

For the sake of comparison with the substance $C_{14}H_{10}O_3$, 1-hydroxy-3-methylxanthone was prepared by Michael's process, and it was soon clear that the substances are identical.

The mechanism of the formation of this substance from phenyl acetate by the action of sodium is probably the following :

The sodium derivative II, which is assumed to be produced (p. 1285) as an intermediate step in the formation of 2-methylbenzo-γ-pyrone, reacts with a second molecule of phenyl acetoacetate, yielding the second intermediate stage (III), and this then undergoes a double internal condensation and is converted into 1-hydroxy-3-methylxanthone :



(II.)

(III.)

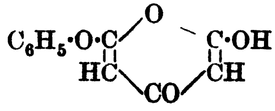
In addition to the above, two substances, not previously observed, are produced during the action of sodium on phenyl acetate and these are dehydracetic acid and a substance (called γ) of the formula $C_{11}H_8O_4$. The formation of dehydracetic acid is additional evidence that phenyl acetoacetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}C_6H_5$, is a product of this decomposition, since this substance might be expected to decompose readily with formation of dehydracetic acid under the high temperature conditions prevailing. The substance (γ), $C_{11}H_8O_4$, is produced in such very small quantity that its constitution could not be determined, and this is the more unfortunate as it exhibits some remarkable properties. It melts at 137°, and although it has acid properties and can be approximately titrated with $N/10$-sodium hydroxide, it does not appear to be a carboxylic acid. It yields sparingly soluble sodium and potassium derivatives and is very readily converted by the action of ammonia into a sparingly soluble substance, $C_{22}H_{17}O_7N$, which melts at 237° and appears to be produced according to the equation:

$$2C_{11}H_8O_4+NH_3=C_{22}H_{17}O_7N+H_2O.$$

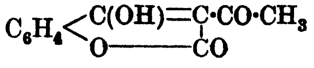
The insolubility of this substance in dilute alkalis seems to indicate that the substance (γ) cannot contain a carboxyl group.

Possibly the substance (γ) is allied to dehydracetic acid, and this is rather indicated by the fact that, like the latter, it yields a deep orange coloration with ferric chloride.

It is suggested that the substance (γ) may be a γ-pyrone derivative and have the constitution IV.



(IV.)



(V.)

This substance might be produced from the product of the condensation of phenyl ethyl malonate and phenyl acetate

$$C_6H_5{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et+CH_3{\cdot}CO_2{\cdot}C_6H_5=$$
$$C_6H_5{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}C_6H_5$$

by the elimination of phenol. Another possibility is that the substance (γ) is closely allied to the lactone (V) of *o*-hydroxybenzoylacetoacetic acid (m. p. 132°), which is obtained when *o*-acetoxybenzoyl chloride reacts with the sodium derivative of ethyl acetoacetate (D.R.P., 102746, 1898. *Chem. Zentr.*, 1899, [ii], 408). In either case, the curious behaviour of the substance (γ) towards ammonia is difficult to explain. Experiments are in progress with a view to the synthesis of substances of the types indicated above, and it is hoped in this way that the identity of the substance (γ) may be revealed.

EXPERIMENTAL.

The Action of Sodium on Phenyl Acetate.

The phenyl acetate employed in these experiments was prepared from pure phenol and excess (70 per cent.) of freshly distilled acetyl chloride by simply heating them together for about an hour; the product was twice fractionated, when the acetate distilled at 194—196° (uncorr.). In the first of the experiments, the decomposition of the phenyl acetate by sodium was carried out in the manner described in the earlier paper (*loc. cit.*) and the formation of ethyl acetate in small quantities and also of considerable quantities of salicylic acid was confirmed. As, however, the main object of the investigation was the determination of the nature of the substances α- (m. p. 68°) and β- (m. p. 138°), which are, in the most favourable circumstances, both formed in yields of not more than 1 per cent., a modification of the conditions of the interaction was made which allows of considerable quantities of material being worked up rapidly.

Sodium (15 grams) was granulated by heating under boiling toluene and shaking vigorously, the toluene decanted, and phenyl acetate (95 c.c.) added. The flask containing the mixture was fitted with a rather wide tube, 3 feet in length, and bent so that half of it acted as a reflux condenser and the other half, connected with a water condenser, served to condense phenyl acetate and other volatile products which might distil over. On warming on the steam-bath, action soon commenced and the temperature rose rapidly until the mixture was in brisk ebullition and liquid distilled into the receiver. When the process had subsided, the dark brown mass was mixed with alcohol and heated on the steam-bath until unchanged sodium had been removed, excess of hot dilute hydrochloric acid was then added and the dark oil washed several times with hot water.* The moist oil was then rapidly distilled under 100 mm., when large quantities of phenol passed over below 130° and, after redistillation, crystallised in the receiver.

The remaining oil was then fractionated under 10 mm. and three principal fractions collected, namely, *A* (b. p. 130—170°), *B* (170—220°), and *C* (220—270°); these were approximately of

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* If this mass is extracted with dilute ammonia, salicylic acid is precipitated on the addition of hydrochloric acid to the alkaline extract.

In one experiment, 6 grams of this acid were obtained from the decomposition by sodium of 100 grams of phenyl acetate, but the quantity is usually not more than 3 grams equal size and they together made up about 15—20 per cent. of the phenyl acetate employed.

2-*Methylbenzo-γ-pyrone, Dehydracetic Acid and the Substance* (γ), $C_{11}H_8O_4$, *of m. p.* 137°.

The fraction *A*, boiling at 130—170°/10 mm., yielded on repeated fractionation a pale yellow oil which distilled at 140—160°/8 mm., and this, on standing in the ice chest, became semi-solid owing to the separation of needles. The whole was filtered with the aid of the pump, the residue washed with a little light petroleum, and recrystallised from this solvent, from which it separated in striated prismatic needles melting at 108—109°, and this substance was readily identified as dehydracetic acid (Found: C=56·8; H=4·7. Calc., C=57·1; H=4·8 per cent.). The oily filtrate, which gave a deep sage green colour when ferric chloride was added to its alcoholic solution, was dissolved in ether and the ethereal solution repeatedly extracted with aqueous potassium carbonate (M) until it gave no coloration with ferric chloride; it was then fractionated, and distilled almost completely at 145—147°/10 mm. On keeping, this oil became semi-solid and, after filtering with the aid of the pump, the crystals were drained on porous porcelain and repeatedly crystallised from light petroleum (b. p. 70—80°), in which the substance is sparingly soluble and from which it separates in long needles resembling phthalic anhydride. It then melted at 69—70° (Found: C=75·1; H=5·2. $C_{10}H_8O_2$ requires C=75·0; H=5·0 per cent.).

The substance α-, described in the earlier communication (*loc. cit.*), melted at 68° and gave C=75·1, 74·5; H=5·3, 5·4 per cent., and a direct comparison showed at once that it is identical with the substance of m. p. 69—70° obtained as just described.

It is explained in the introduction that this substance is identical with 2-methylbenzo-γ-pyrone, which Block and Kostanecki (*loc. cit.*) obtained from *o*-methoxybenzoylacetone,

$$CH_3{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3,$$

by boiling with hydriodic acid, which they describe as melting at 70—71°. Both specimens show the characteristic reaction described in the earlier communication (*loc. cit.*, p. 489), namely, an intense carmine coloration which develops on warming with methyl-alcoholic potassium hydroxide, and an intimate mixture of the two preparations was found to melt quite sharply at 69—70°.

The potassium carbonate extract (M, see above) was acidified and extracted with ether, the extract dried over calcium chloride and evaporated, when a syrup remained which soon crystallised.

The crystals were left in contact with porous porcelain until free from oily impurity and the colourless residue was crystallised from methyl alcohol,* when glistening needles were obtained which melted at 137° (Found: $C=64{\cdot}9$; $H=4{\cdot}1$. $C_{11}H_8O_4$ requires $C=64{\cdot}7$; $H=3{\cdot}9$ per cent.). This substance (γ)—the constitution of which is briefly discussed in the introduction, p. 1287—dissolves readily in warm dilute sodium carbonate solution or ammonia, but when it is mixed with rather concentrated sodium hydroxide solution, it does not dissolve but changes in appearance, yielding a sparingly soluble sodium derivative which dissolves readily in a few drops of boiling water and separates as a voluminous mass of needles. The substance (γ) dissolves readily in methyl-alcoholic potassium hydroxide, and on cooling crystals of a sparingly soluble potassium derivative separate. An attempt was made to titrate the substance with $N/10$-sodium hydroxide, using phenolphthalein, at the temperature of the steam-bath, but the end-point was not very sharp; 0·3958 neutralised 0·0790NaOH, whereas this amount of a substance, $C_{11}H_8O_4$, combining with 1NaOH should neutralise 0·0776NaOH.

On acidifying the liquid from the titration, the substance (γ) separated immediately in needles. The solution of this substance in methyl alcohol gives, on the addition of ferric chloride, a deep orange coloration closely resembling that produced by dehydracetic acid. It dissolves in concentrated sulphuric acid to a colourless solution, and there is no visible change on the addition of concentrated nitric acid. The most characteristic property of the substance is its behaviour with ammonia. It dissolves readily in dilute ammonia and, if concentrated ammonia is then added and the liquid heated or evaporated, a very sparingly soluble substance separates as a mass of needles. This was collected, washed with water, and dried at 110°, when it melted sharply at 237°. It was insoluble in dilute sodium carbonate solution even on warming and was also insoluble in cold dilute sodium hydroxide solution, but on boiling it passed into solution with evolution of ammonia, and on acidifying a crystalline substance separated, the quantity of which was not sufficient for examination. The analysis of the substance of m. p. 237° gave $C=65{\cdot}2$; $H=4{\cdot}5$; $N=3{\cdot}4$, whereas $C_{22}H_{17}O_7N$ requires $C=64{\cdot}9$; $H=4{\cdot}2$; $N=3{\cdot}4$ per cent.

This substance is therefore to be produced from the substance (γ) according to the equation:

$$2C_{11}H_8O_4+NH_3=C_{22}H_{17}O_7N+H_2O.$$

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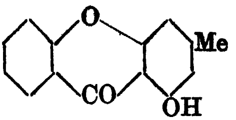
* The mother-liquors contain considerable quantities of salicylic acid and a small quantity of dehydracetic acid.

1-*Hydroxy*-3-*methylxanthone*,



When the portion of the product of the action of sodium on phenyl acetate boiling at 220—270°/10 mm. (p. 1288) was allowed to stand, it gradually deposited crystals, and crystallisation was greatly facilitated by dissolving the whole in three volumes of boiling methyl alcohol and allowing the solution to stand for a couple of days in the ice chest. The crystals were collected * and recrystallised from methyl alcohol, when lemon-yellow needles separated, which melted at 141°, and, as explained in the introduction (p. 1286), consisted of 1-*hydroxy*-3-*methylxanthone* (Found: C=74·5, 74·3; H=4·6, 4·5. Calc., C=74·3; H=4·4 per cent.).

This substance is identical with the substance of melting point 138° described in the earlier communication (*loc. cit.*), but the specimen was then obviously not quite pure, since the analytical figures (C=73·5; H=4·6) were inaccurate and the melting point was low. 1-Hydroxy-3-methylxanthone is very sparingly soluble in cold methyl alcohol and not readily so on boiling, but it is much more soluble in ethyl alcohol. It dissolves readily in boiling acetone, and crystallises splendidly from this solvent in glistening, pale yellow needles; it is also very soluble in benzene, but sparingly soluble in boiling light petroleum, from which it separates in colourless needles. It is insoluble in, and is not coloured by, dilute ammonia, but is turned orange by sodium hydroxide owing to the formation of the sodium derivative, which is very sparingly soluble even in boiling water. It dissolves in sulphuric acid to a bright yellow solution which does not appear to change on heating on the steam-bath. It does not yield a semicarbazone when semicarbazide acetate is added to the alcoholic solution. Michael (*loc. cit.*, p. 1286) has pointed out that 1-hydroxy-3-methylxanthone yields a colourless acetyl derivative (m. p. 152°) when it is digested with anhydrous sodium acetate and acetic anhydride, but the following experiment shows that the substance is not easily acetylated. It dissolves readily in acetic anhydride to a yellow solution, and if this is boiled for several minutes and then most of the acetic anhydride distilled off, the liquid deposits yellow crystals which, after crystallisation from methyl alcohol, melt at 138—140° and consist of the unchanged substance.

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* A further quantity may be obtained by distilling off the methyl alcohol, fractioning the residue, collecting between 210° and 250°/10 mm., and treating again with methyl alcohol, but, on repeating this process, a large amount of a viscid syrup is obtained which could not be made to crystallise.

The Potassium Derivative, $C_{14}H_9O_3K$.—It is mentioned in the earlier paper (*loc. cit.*) that the substance of melting point 138° yields a fine yellow, crystalline compound when it is warmed with alcoholic potassium hydroxide. In order to examine this characteristic derivative, hydroxymethylxanthone was dissolved in boiling methyl alcohol and methyl-alcoholic potassium hydroxide (25 per cent.) added to the saturated solution, when a deep orange colour immediately developed and crystals separated. The precipitate was collected, washed with methyl alcohol, in which it is very sparingly soluble, dried at 100° and analysed (Found : $C=63{\cdot}0$; $H=3{\cdot}2$; $K=14{\cdot}7$. $C_{14}H_9O_3K$ requires $C=63{\cdot}6$; $H=3{\cdot}4$; $K=15{\cdot}4$ per cent.).

This potassium derivative is very sparingly soluble even in boiling water, and is decomposed by dilute hydrochloric acid, with separation of hydroxymethylxanthone.

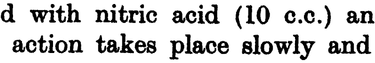
Methyl Ether of 1-Hydroxy-3-methylxanthone.

Considerable difficulty was experienced in preparing this substance owing to the fact that hydroxymethylxanthone is not readily methylated under the usual conditions. Thus the crystalline sodium derivative, suspended in methyl alcohol, may be boiled for hours with methyl iodide without apparent change. Methyl sulphate also does not readily react with the sodium derivative, but repeated treatment with methyl-alcoholic potassium hydroxide and methyl sulphate finally lead to the desired result. Hydroxymethylxanthone (1 gram), suspended in methyl alcohol, was mixed with a solution of sodium hydroxide (2 grams) in methyl alcohol and then methyl sulphate (6 grams) added. After heating on the steam-bath for fifteen minutes, successive quantities of methyl alcoholic potassium hydroxide (25 per cent.) and methyl sulphate were added until the product was only faintly yellow. On adding water, a pale yellow, crystalline substance separated, which, since it gave in solution in methyl alcohol a deep green coloration with ferric chloride, clearly contained unchanged hydroxymethylxanthone. The whole was again treated with methyl-alcoholic potassium hydroxide and methyl sulphate and the product collected, washed well, and crystallised several times from benzene, from which the methyl ether separated in colourless prisms melting at 152° (Found : $C=74{\cdot}8$; $H=5{\cdot}0$; $MeO=12{\cdot}2$. $C_{15}H_{12}O_3$ requires $C=75{\cdot}0$; $H=5{\cdot}0$; $MeO=12{\cdot}9$ per cent.).

This methyl ether is sparingly soluble in methyl alcohol even on boiling and separates, on cooling, as a voluminous mass of colourless needles; the methyl-alcoholic solution gives no coloration on the addition of ferric chloride. It is readily soluble in benzene and separates in groups of needles, but it crystallises best from ethyl acetate, in which it is rather sparingly soluble in the cold but dissolves readily on boiling, and from which it separates as a felted mass of glistening needles. It dissolves in cold concentrated sulphuric acid with a deep yellow colour, the addition of nitric acid intensifies the colour, and after heating at 50° for a few minutes, dilution with water gives a deep yellow, crystalline precipitate of a mixture of nitro-derivatives. It is curious that the methyl ether is decomposed by boiling with methyl-alcoholic potassium hydroxide. The solution in this reagent was at first colourless, but on boiling and concentrating gradually became deep orange and an orange substance separated in satiny needles. When this was collected and decomposed by dilute hydrochloric acid, it yielded 1-hydroxy-3-methylxanthone, which, after crystallising from methyl alcohol, melted at 141°.

A small quantity of a colourless substance, contained in the alkaline solution, separated on acidification and gave in methyl-alcoholic solution a purple-black coloration on the addition of ferric chloride.

2- *and* 4-*Nitro*-1-*hydroxy*-3-*methylxanthones*,



$$C_6H_4<\genfrac{}{}{0pt}{}{O}{CO}>C_6HMe(NO_2)\cdot OH.$$

1-Hydroxy-3-methylxanthone is very readily attacked by concentrated nitric acid, especially on warming at 50°, and the best way to study the action is to use dilute nitric acid in the following manner. The substance (2 grams), ground to a paste with water (30 c.c.), is gradually mixed with nitric acid (10 c.c.) and heated on the steam-bath, when action takes place slowly and is completed by the addition from time to time of equal parts of nitric acid and water. After two hours, water is added, the yellow precipitate collected, washed well, dried on porous porcelain, and boiled with alcohol, when a considerable amount remains undissolved and, after filtering off and washing with hot alcohol, this consists of the almost pure 4-nitro-derivative (m. p. 275°).

The filtrate, on standing, deposits a small quantity of the 4-nitro-derivative and then, on concentrating and leaving, bundles of curved needles of the 2-nitro-derivative (m. p. 170°) separate. The mother-liquor from this substance gives, on further concentration, ochre warts which melt at about 117°, but this substance or mixture was not further examined.

4-*Nitro*-1-*hydroxy*-3-*methylxanthone* is characterised by being very sparingly soluble in the usual organic solvents; it dissolves, however, appreciably in boiling methyl ethyl ketone or glacial acetic acid and separates in bright yellow laminæ (Found: C=62·1; H=3·3; N=5·3. $C_{14}H_9O_5N$ requires C=62·0; H=3·3; N=5·2 per cent.). The solution of this substance in alcohol gives on the addition of ferric chloride a port wine coloration, and warming with methyl-alcoholic potassium hydroxide yields an orange, crystalline potassium derivative. The 4-nitro-derivative dissolves remarkably readily in cold concentrated sulphuric acid, apparently with the formation of an oxonium sulphate, since on adding an equal volume of water and heating a clear solution is obtained. The further addition of water produces a colourless, chalky precipitate which becomes yellow on boiling. The 4-nitro-derivative is insoluble in cold nitric acid, but dissolves on warming and, on boiling, oxidation takes place readily with formation of a brown solution, from which a yellow, crystalline acid separates on cooling.

2-*Nitro*-1-*hydroxy*-3-*methylxanthone* is much more readily soluble in organic solvents than the 4-nitro-derivative, and separates from boiling acetone in voluminous masses of lemon-yellow needles (Found: C=62·3; H=3·4; N=5·2. $C_{14}H_9O_5N$ requires C=62·0; H=3·3; N=5·2 per cent.). The alcoholic solution gives, on the addition of ferric chloride, a deep claret coloration and methyl-alcoholic potassium hydroxide added to the alcoholic solution precipitates a sparingly soluble potassium derivative, which dissolves in boiling water and crystallises in needles.

The author is greatly indebted to Professor R. Robinson for several valuable suggestions made during the course of this research.

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[*Received, June 7th,* 1921.]

CXLVII.—*The Doebner-Miller Quinaldine Synthesis.*

By WILLIAM HOBSON MILLS, JOHN EDMUND GUY HARRIS, and HERBERT LAMBOURNE.

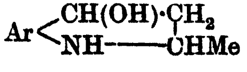
IN the well-known Doebner and von Miller synthesis of quinaldine by the condensation of aniline with acetaldehyde under the influence of hydrochloric acid, the hydrogen produced according to equation

$$C_6H_7N + 2C_2H_4O = C_{10}H_9N + 2H_2O + 2H$$

is generally supposed to be consumed largely in the production of tetrahydroquinaldine. We were therefore surprised to find in preparing a quantity of quinaldine by a method that was essentially that of Doebner and von Miller that very little, if any, tetrahydroquinaldine was produced. The secondary bases, which were generated in considerable quantity and formed the chief constituents of the volatile by-products accompanying the quinaldine, contained, however, a compound which very closely resembled tetrahydroquinaldine in composition and general character. This substance, which formed about half the total quantity of the secondary bases, proved on investigation to be *n*-butylaniline.

The process which we employed differed from that of Doebner and von Miller in that (i) commercial acetaldehyde was used instead of paraldehyde, the mixture being allowed to stand at 0° for half an hour before heating, and (ii) the heating was carried out in the presence of a certain amount of zinc chloride, a modification which was found to increase the yield of quinaldine. The resulting mixture of bases was treated with nitrous acid to separate the secondary bases as nitroso-compounds. The secondary bases regenerated from these were divided by fractional distillation into two fractions boiling at 204° and 236—237° respectively. The former was identified as monoethylaniline, which Doebner and von Miller had already recognised as a by-product of this reaction (*Ber.*, 1884, **17**, 1669). The latter we supposed would be tetrahydroquinaldine. However, its crystalline derivatives were quite distinct from those of tetrahydroquinaldine; for example, the benzoyl derivative melted at 55°, whereas benzoyltetrahydroquinaldine melts at 118°. Analysis pointed to the formula $C_{10}H_{15}N$, indicating that the base was probably either ethylaminoethylbenzene or one of the butylanilines. It proved to be *n*-butylaniline, its crystalline derivatives showing exact correspondence with those of a specimen of *n*-butylaniline prepared for comparison. The occurrence of this substance is easily explained; it is evidently formed by reduction of crotonylideneaniline, $CH_3{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C_6H_5$, proceeding from crotonaldehyde formed by condensation of the acetaldehyde.

When acetaldehyde is allowed to act on a solution of a primary aromatic base in dilute hydrochloric acid, the "aldol bases," discovered by von Miller and Plöchl (*Ber.*, 1896, **29**, 1467), are formed. These compounds, which result from the condensation of one molecule of base and two of aldehyde with the elimination of water, were studied by H. O. Jones and a series of co-workers (T., 1910, **97**, 632; 1911, **99**, 334; 1912, **101**, 1376, 1389). As a result of these investigations, formulæ of the type



$$\mathrm{Ar}\begin{cases}\mathrm{CH(OH){\cdot}CH_2} \\ \mathrm{NH{-\!-\!-}CHMe}\end{cases}$$

were assigned to these compounds, and it was shown that, on heating alone or with acids, they lost water and were converted into a mixture of a quinaldine base with its tetrahydro-derivative.

The aldol bases are therefore in all probability intermediate products in the quinaldine synthesis. When the decomposition of a compound of this type into a quinaldine base and water takes place in the absence of more reducible compounds, tetrahydroquinaldine is formed in quantity. When, however, the aldol base decomposes under the conditions of the quinaldine synthesis here described, the hydrogen given up is absorbed mainly by the Schiff's bases, ethylideneaniline and crotonylideneaniline, present in the reaction mixture, with the formation of ethylaniline and *n*-butylaniline, and the production of tetrahydroquinaldine, which can scarcely be supposed to be entirely suppressed, is relatively so small that we have been unable to isolate any of this base from the products of the reaction.

The tertiary bases also contain a previously undescribed by-product, the formation of which affords some additional information regarding the processes taking place in this synthesis. This is 6-ethylquinaldine.

By distillation, the tertiary bases can be resolved into two fractions, the main quinaldine fraction boiling at 241—243° and a much smaller fraction boiling at about 280°, of which the main constituent is a base characterised by a sparingly soluble dichromate. Analysis of this base pointed to the formula $C_{12}H_{13}N$, and the fact that no corresponding compound is formed when para-substituted anilines, such as *p*-toluidine or *p*-phenetidine, are employed instead of aniline, together with the probability that acetaldehyde, like formaldehyde, would be capable of condensing with aniline in the para-position, suggested that it might be 6-ethylquinaldine. This view was confirmed by the result of oxidising the base with chromic acid; 2-methylquinoline-6-carboxylic acid was produced. The synthesis of 6-ethylquinaldine from *p*-aminoethylbenzene was therefore undertaken, and on comparison of this substance with the base contained in the fraction boiling at 280° it was found that the two compounds were identical. It would thus appear that, whereas under the conditions of this synthesis the acetaldehyde for the most part attacks the amino-group of aniline, forming ethylideneaniline, crotonylideneaniline, the aldol base, etc., it also reacts to some extent with the hydrogen atom in the para-position of the benzene nucleus. Possibly the compounds $CH_3{\cdot}CH(OH){\cdot}C_6H_4{\cdot}NH_2$ and $CH_2{:}CH{\cdot}C_6H_4{\cdot}NH_2$ are the intermediate products to which the formation of ethylquinaldine is due. That such compounds should be produced by processes analogous to those which bring about the formation of diaminodiphenylmethane from aniline and formaldehyde is very probable. Their conversion, however, into 6-ethylquinaldine, which would involve the reduction of the vinyl to the ethyl group, would demand reducing agencies of considerable intensity, and this consideration suggests that the ethylquinaldine might rather be formed from the ethylaniline present in the reaction mixture by a process involving condensation with acetaldehyde accompanied by intramolecular migration of the ethyl group. It is proposed to investigate this question further.

EXPERIMENTAL.

Preparation of Quinaldine.

Acetaldehyde (350 grams) in concentrated solution (about 75 per cent.) was added slowly to a well-stirred mixture of aniline hydrochloride and hydrochloric acid prepared from aniline (300 c.c.) and concentrated hydrochloric acid (1200 c.c.) cooled in ice-water. After leaving for thirty minutes, zinc chloride (240 grams) was added and the solution was heated gently under reflux until the vigorous reaction began. When this had subsided, the liquid was boiled for four to six hours, poured on to excess of slaked lime, and the mixture distilled with steam until 12 litres of distillate had been collected. The crude oil (about 250 c.c.) was separated from the aqueous layer and the dissolved bases were extracted from the latter with a little chloroform.

Separation of the Secondary Bases.

The crude oil (500 c.c.) was dissolved in dilute sulphuric acid and a slight excess of sodium nitrite was added to the ice-cooled solution. The secondary nitrosoamines which separated were at once extracted with ether. The aqueous layer was then heated on the water-bath, made alkaline with sodium hydroxide, and the tertiary bases were distilled with steam.

The secondary bases were recovered from the nitrosoamines by treatment in the usual manner with tin and hydrochloric acid. They were then fractionally distilled and thus separated into two approximately equal fractions, (*a*) ethylaniline, boiling at 204°, and (*b*) *n*-butylaniline, boiling at 236—237°.

Identification of Ethylaniline.

The following derivatives of the secondary base boiling at 204° were prepared by the usual methods and were found by careful comparison, and especially by the determination of the melting points of the mixtures, to be identical with the corresponding derivatives of monoethylaniline.

p-*Toluenesulphonylethylaniline* (Found: S=11·76. Calc., S=11·64 per cent.).—Recrystallised from light petroleum, this preparation, the control preparation, and the mixture of the two melted at 68—69°. Since the melting point previously recorded for this compound was 87—88° (Otto, *J. pr. Chem.*, 1893, [ii], **47**, 371), it appeared that we had obtained a new meta-stable form of the substance and further observations confirmed this. A specimen of melting point 68—69° which had been kept corked in a tube for about two years was fused by immersion in a bath at 74°. The tube was then opened and the liquid, still at 74°, was inoculated with a minute crystal of the form melting at 87—88° from a specimen which had been prepared for us by Mr. A. S. Russell. It crystallised rapidly and completely, and as the temperature of the bath was gradually raised, melted again at 87—88°.

Benzoylethylaniline (Found: C=80·1; H=6·7. Calc., C=80·0; H=6·7 per cent.).—The melting point of this preparation, of the control preparation, and of the mixture of the two was 54°. Hess (*Ber.*, 1885, **18**, 687) gives 60° as the melting point of benzoylethylaniline.

Identification of n-*Butylaniline.*

The secondary base boiling at 236—237° had the composition of *n*-butylaniline (Found: C=80·67; H=10·1. Calc., C=80·53; H=10·06 per cent.). Its crystalline derivatives were found to be identical with those of a specimen of *n*-butylaniline prepared for comparison.

Benzoyl-n-*butylaniline* (Found: C=80·42; H=7·70. $C_{17}H_{19}ON$ requires C=80·57; H=7·50 per cent.).—This substance prepared from the by-product base, the control preparation from *n*-butylaniline synthesised directly from aniline, and the mixture of the two preparations melted at 55°.

n-*Butylaniline Hydrochloride.*—A solution of the base in one equivalent of hydrochloric acid was evaporated and the crystalline residue recrystallised from alcohol and ether (Found: HCl=19·8. $C_{10}H_{15}N,HCl$ requires HCl=19·7 per cent.). The salt, the control preparation, and the mixture melted at 110°.

n-*Butylaniline Oxalate.*—This salt, the control preparation, and the mixture melted and decomposed at 146°.

Tetrahydroquinaldine hydrochloride is considerably less soluble than the hydrochloride of *n*-butylaniline, and it was found comparatively easy by fractional crystallisation from alcohol and ether to isolate the former salt from the hydrochlorides prepared from artificial mixtures of the two bases. A careful examination of all the higher fractions of the secondary bases (tetrahydroquinaldine boils at 250°) by this method failed to give any indication of the presence of tetrahydroquinaldine.

A definite proof of the presence of this base among the secondary bases occurring as by-products in the Doebner and von Miller synthesis of quinaldine appears not yet to have been obtained. Doebner and von Miller, in claiming to identify it, merely state (*Ber.*, 1884, **17**, 1669) that tetrahydroquinaldine "wurde in Form seiner Nitrosoverbindung, durch sein Verhalten gegen Eisenchlorid und seine sonstigen Eigenschaften nachgewiesen." They found that tetrahydroquinaldine gave a red colour with ferric chloride. Freshly prepared *n*-butylaniline gives a green colour with this reagent, but with specimens of the base that had been kept a few weeks a red colour was obtained.

The Tertiary Bases.

From one litre of crude quinaldine 630 c.c. of tertiary bases were obtained. These were found on fractionation to contain, besides quinaldine, a small quantity (about 7 grams) of a base boiling at 276—282°. The molecular weight of this base was found by analysis of its platinichloride to be 176. The ethiodide, prepared by heating equimolecular quantities of the base and ethyl iodide under pressure at 100°, was found to contain 38·94 per cent. of iodine, indicating a molecular weight of 170 for the base. It was therefore suspected that this fraction of higher boiling point consisted chiefly of 6-ethylquinaldine, the molecular weight of which is 171. It was found that the base could be purified through its dichromate, which crystallised well from hot water (the solution should not be heated above 65°) and melted constantly at 134°. The base recovered from the dichromate had the composition of ethylquinaldine (Found: C=84·07; H=7·6; N=8·29. $C_{12}H_{13}N$ requires C=84·2; H=7·6; N=8·2 per cent.). On oxidation, it gave 2-methylquinoline-6-carboxylic acid, and was therefore 6-ethylquinaldine. A solution of the base (10 grams) in dilute sulphuric acid was heated for three hours on the water-bath with chromic anhydride (30 grams) dissolved in water (100 c.c.) and sulphuric acid (40 c.c.) (compare Miller, *Ber.*, 1890, **23**, 2263). The chromic salts were removed by precipitation with ammonia and the filtrate was evaporated on the water-bath. The acid was deposited in crystalline crusts during the evaporation through the dissociation of its ammonium salt, and was purified by washing with water and recrystallisation from alcohol. It consisted of needles darkening at 235° and melting at 260° (Found: C=70·5;

$H=5{\cdot}06$. $C_{11}H_9O_2N$ requires $C=70{\cdot}6$; $H=4{\cdot}82$ per cent.). The acid thus obtained agreed exactly in properties with a specimen of 2-methylquinoline-6-carboxylic acid prepared by the oxidation of *p*-toluquinaldine (Miller, *Ber.*, 1890, **23**, 2263) and a mixture of the two preparations melted at 260°.

Synthesis of 6-Ethylquinaldine.

As 6-ethylquinaldine had not been previously described, its preparation from *p*-aminoethylbenzene and acetaldehyde was undertaken.

To concentrated hydrochloric acid (136 c.c.) was added *p*-aminoethylbenzene (49 grams) and then acetaldehyde (45 grams) in 75 per cent. solution, the mixture being kept cool with ice. After half an hour zinc chloride (33 grams) was introduced and the solution was boiled under reflux for four hours. It was then diluted and made alkaline with sodium hydroxide and the bases were distilled with steam. The product left after removal of the secondary bases and any unchanged aminoethylbenzene with nitrous acid in the manner described above (p. 1297) was distilled and the ethylquinaldine was thus obtained as an oil boiling at 276—279° (uncorr.) (Found: $C=83{\cdot}7$; $H=7{\cdot}63$. $C_{12}H_{13}N$ requires $C=84{\cdot}16$; $H=7{\cdot}65$ per cent.).

The boiling point observed for the base with the thread of the thermometer completely immersed in the vapour was 288°. The dichromate melts at 134° and a mixture of the dichromate from the base synthesised directly, and that from the ethylquinaldine isolated from the crude quinaldine melted also at 134°. Solutions of the base in hydrochloric acid give crystalline double salts with mercuric chloride and with zinc chloride melting at 155° and 167° respectively.

6-Ethylquinaldine Methiodide.—Equimolecular quantities of the base and methyl iodide were warmed at 50° under reflux for four hours. The resulting solid yellow mass was recrystallised from rectified spirit. The methiodide was thus obtained in yellow needles melting at 214° [Found: $I=40{\cdot}55$ (from synthetic base); $40{\cdot}72$ (from by-product base). $C_{13}H_{16}NI$ requires $I=40{\cdot}57$ per cent.]. The mixture of the methiodides from the two sources melted at 214°.

Our thanks are due to Mr. G. N. Nicklin and Mr. W. N. Hoyte for valuable assistance in connexion with the preparation of 6-ethylquinaldine and the comparison of this compound with the tertiary base of high boiling-point contained in crude quinaldine.

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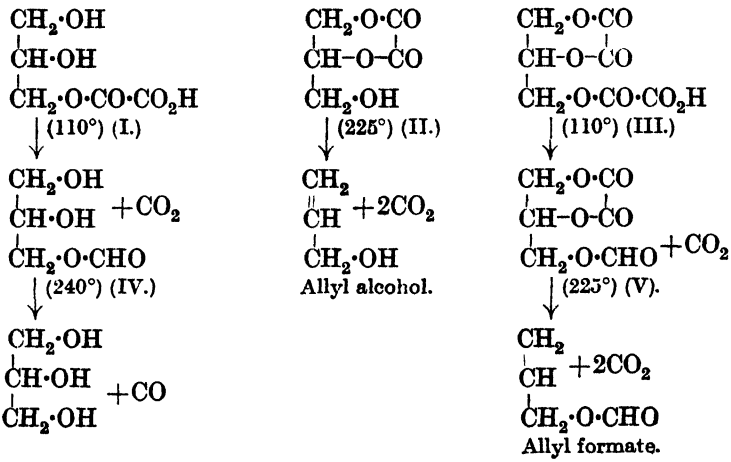
CXLVIII.—*The Preparation of some Allyl Compounds.*

By Samuel Coffey and Charles Frederick Ward.

For certain researches which are in progress in this laboratory the authors required considerable quantities of allyl chloride, and the present communication is the outcome of a study of the methods of preparing this compound.

The well-known process of Tollens for the production of allyl alcohol (*Annalen*, 1870, **156**, 129) is open to very serious objections and is probably based on a false conception of the reaction. A very large excess of glycerol is used and the amount of oxalic acid lost as carbon monoxide is also very large, consequently the yield is very poor. Chattaway (T., 1914, **105**, 151; 1915, **107**, 407) demonstrated that it was essentially by the decomposition of a dioxalin that allyl alcohol was produced and that the reactions between glycerol and oxalic acid appeared to be represented by the following scheme :



$$\begin{array}{lll}
\begin{array}{l} CH_2{\cdot}OH \\ CH{\cdot}OH \\ CH_2{\cdot}O{\cdot}CO{\cdot}CO_2H \end{array} &
\begin{array}{l} CH_2{\cdot}O{\cdot}CO \\ CH{-}O{-}CO \\ CH_2{\cdot}OH \end{array} &
\begin{array}{l} CH_2{\cdot}O{\cdot}CO \\ CH{-}O{-}CO \\ CH_2{\cdot}O{\cdot}CO{\cdot}CO_2H \end{array} \\
\downarrow (110^\circ)\ (I.) & \downarrow (225^\circ)\ (II.) & \downarrow (110^\circ)\ (III.) \\
\begin{array}{l} CH_2{\cdot}OH \\ CH{\cdot}OH \\ CH_2{\cdot}O{\cdot}CHO \end{array} + CO_2 &
\begin{array}{l} CH_2 \\ CH \\ CH_2{\cdot}OH \end{array} + 2CO_2 &
\begin{array}{l} CH_2{\cdot}O{\cdot}CO \\ CH{-}O{-}CO \\ CH_2{\cdot}O{\cdot}CHO \end{array} + CO_2 \\
\downarrow (240^\circ)\ (IV.) & \text{Allyl alcohol.} & \downarrow (225^\circ)\ (V). \\
\begin{array}{l} CH_2{\cdot}OH \\ CH{\cdot}OH \\ CH_2{\cdot}OH \end{array} + CO & &
\begin{array}{l} CH_2 \\ CH \\ CH_2{\cdot}O{\cdot}CHO \end{array} + 2CO_2 \\
 & & \text{Allyl formate.}
\end{array}$$

The oxalins I, II, and III are initially formed in varying proportions according to the conditions of the experiment. At higher temperatures (110°) the hydrogen oxalins give carbon dioxide and formins (IV and V). Dioxalin (II) and monoformin dioxalin (V), at higher temperatures still (220—225°), decompose into carbon dioxide and allyl alcohol and allyl formate respectively, whilst at still higher temperatures (240°) monoformin (IV) gives glycerol and carbon monoxide. Formic acid is produced by the action of an excess of oxalic acid on the formins and distils during the second stage of the reaction. From this it is apparent that a relatively large amount of oxalic acid must be used in the preparation of allyl alcohol.

Chattaway (*loc. cit.*) drew these conclusions partly from a study of the action of ammonia and aniline on the products of the reaction and partly from the properties of the ethyl oxalates; the results of comparative experiments given below completely confirm the above scheme in every detail.

The experiments also clearly demonstrated the four consecutive reactions, and it was possible to convert nearly the whole of the glycerol in one operation into allyl alcohol and to account for more than 90 per cent. of the oxalic acid as free and combined formic acid, carbon dioxide, and water. The net loss, therefore, is negligible.

From the point of view of the student the usual methods of preparing formic acid and allyl alcohol are very uninteresting and unsatisfactory with regard to yield, time, and manipulation. Also the simple equation given in the text-books gives no clue as to where the loss occurs.

The method given below would seem to be far superior to the old method as a laboratory experiment. In the course of one day the student could, in one operation, obtain about 40 grams of formic acid as an approximately 50 per cent. solution, and 100 grams of pure allyl alcohol and at the same time follow the whole reaction and account for all his materials.

Allyl chloride is by far the cheapest allyl haloid, but the methods of preparing it leave much to be desired. Eltekow's method (*J. Russ. Phys. Chem. Soc.*, 1882, **14**, 394) is long and gives only a 50 per cent. yield, whilst the action of phosphorus trichloride on the alcohol gives mainly phosphorous esters and only 10—20 per cent. of allyl chloride. More recently, Bruylant (*Rec. trav. chim.*, 1909, **28**, 247) has improved the preparation by heating allyl alcohol and hydrogen chloride under pressure, but he gives no details of yield. Aschan (*Finska. Chem. Med.*, 1918, 3 pp.) finds that allyl chloride is obtained in good yield from allyl formate and hydrogen chloride in the presence of anhydrous zinc chloride. The authors' experiments show that, in the presence of condensing agents, the time of interaction of hydrogen chloride and allyl alcohol may be considerably shortened, but as a rule the yield of allyl chloride is very little better than that given by the older methods. The only condensing agent which is of any practical use is zinc chloride.

EXPERIMENTAL.

Preparation of Allyl Alcohol, Allyl Formate, and Formic Acid.

Pure, hydrated, finely divided oxalic acid (500 grams) and anhydrous glycerol (250 grams) are mixed in a litre flask which is connected with a condenser and receiver. The latter is connected with a water-pump and exhausted to about 120—100 mm. The flask is then gently warmed. At about 60° (thermometer in the liquid) the mixture boils vigorously, becomes homogeneous, and water (more than 100 grams) distils. This is the first stage of the reaction, the formation of the oxalins I, II, and III, and usually takes one hour. The pressure then rapidly rises to 480 mm. and the thermometer remains stationary at 105—110° for some time. The vigorous ebullition ceases, a rapid effervescence of carbon dioxide sets in, and formic acid distils over with more water. There is no frothing if pure materials are used and the pressure is maintained below 500 mm. After one to one and a half hours, the pressure in the apparatus slowly falls to about 120 mm.; this indicates the end of the second stage, namely, the production of formins IV and V from the oxalins by loss of carbon dioxide and their subsequent decomposition into oxalins and formic acid by excess of oxalic acid. The temperature also rises to 190°, when distillation and evolution of gas almost cease. Quite suddenly, at 195—200°, the pressure increases rapidly. The receiver is then changed and the distillation carried on at the ordinary pressure. Carbon dioxide is again rapidly evolved, contaminated with some carbon monoxide and a negligible quantity of allyl formate. Allyl alcohol and allyl formate distil over together and the temperature remains stationary at 225° until distillation ceases, showing the end of the third stage of the reaction. The temperature then rises to 240°, when there is a rapid evolution of almost pure carbon monoxide. The last reaction ceases abruptly after about five minutes, and the colourless residue (80 grams) consists of glycerol. During the last two stages of the reaction the apparatus should be connected with a wash-bottle containing water, and the gases led into an efficient draught-chamber. If the rate of decomposition is allowed to become too rapid, a large amount of glycerol is liable to distil over. It will be seen from the above description that the changes on the manometer and the thermometer are accurate criteria of the transitions between the various stages of the reaction.

To obtain pure allyl alcohol, the crude allyl alcohol–formate mixture (150 grams) is boiled under reflux with 750 c.c. of 10 per cent. sodium hydroxide solution for one hour and fractionated through a long column. All the allyl alcohol passes over below 98° and the distillate is dried with small quantities of anhydrous potassium carbonate. It is then distilled and should give 100 grams of pure allyl alcohol, b. p. 95—97°.

To obtain allyl formate, the crude allyl alcohol–formate mixture is washed several times with small quantities (20 c.c.) of water to remove allyl alcohol, and the insoluble ester dried over anhydrous calcium chloride. This on distillation gives a yield of pure ester, b. p. 82—83°, corresponding with 70 per cent. of the crude alcohol–formate mixture. The washings may be worked up for allyl alcohol in the usual manner.

Allyl formate may also be obtained by fractionating the crude product several times, but in this case only a 50 per cent. yield can be obtained. The formic acid in the first aqueous distillate (stages I and II) may be recovered either as a formate or as formic acid in the usual manner.

Thus, in one operation, 40 grams of formic acid and 100 grams of pure allyl formate, or about 100 grams of allyl alcohol, can be obtained from 250 grams of glycerol and 500 grams of hydrated oxalic acid.* The residue of glycerol (80 grams) is quite suitable for further use.

The following table gives the results of comparative experiments performed exactly as described with different initial concentrations of glycerol and oxalic acid. It will be seen that these results are in complete accord with those required by the above reaction scheme, and may be summarised as follows.

1. The yield of allyl alcohol calculated on the glycerol actually used is always nearly theoretical.

2. As the amount of oxalic acid increases, the yield of allyl formate in comparison with allyl alcohol also increases. This is to be expected, because the larger amounts of oxalic acid are favourable to the production of dioxalin hydrogen oxalate (III), as is readily shown by a comparison of the amount of the alcohol–formate mixture with the yield of allyl formate. This was actually proved by isolating the allyl formate.

3. With increase of oxalic acid, the amount of free formic acid increases.

4. With increase of oxalic acid, the amount lost as carbon monoxide is diminished. This passes through a minimum in experi-

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* There is no necessity to use anhydrous oxalic acid in the above preparation (see Chattaway, *loc. cit.*), as all the water of crystallisation distils over during stages I and II. This effects a saving of several hours in the duration of the experiment.

ment 4, as in experiment 5 the loss increases again. In this experiment the amount of oxalic acid is relatively very large, and no doubt di- and tri-hydrogen oxalins would be produced in appreciable quantities, giving the corresponding formins and ultimately glycerol and carbon monoxide.

Results of Comparative Experiments.

	1.	2.	3.	4.	5.
	Grams.	Grams.	Grams.	Grams.	Grams.
Glycerol taken	400	350	350	250	200
Oxalic acid taken ...	275	350	500	500	500
Alcohol-formate mixture	40	88	110	150	110
Allyl alcohol	32	65	85	95	80
Free formic acid	7	13	25	36	42
Glycerol recovered ...	215	230	210	80	60
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Percentage of oxalic acid lost after calculating for free and combined formic acid, CO_2 and H_2O	50	30	28	10	20
Percentage of formate in alcohol-formate mixture	35	40	60	70	75

The amount of carbon monoxide was relatively much larger with smaller amounts of oxalic acid. The quantitative results are not given, but it may be stated that in experiment 3 the ratio $CO : CO_2$ rapidly exceeded unity, whilst in experiment 4 this ratio was not reached until all the allyl alcohol had distilled. In experiment 5 the amount of carbon monoxide was larger for the reason already given.

Preparation of Allyl Chloride.

The best results were obtained as follows:

Allyl alcohol (46 grams) and anhydrous zinc chloride (20 grams) were mixed in a distillation flask immersed in a water-bath at 75—82°, and hydrogen chloride was passed into the mixture. The gas was rapidly absorbed and a liquid distilled. The end of the reaction was indicated by hydrogen chloride issuing from the end of the condenser. The crude distillate gave on fractionation: allyl chloride (35 grams) corresponding with a 60 per cent. yield, and 10 grams of diallyl ether, b. p. 90—95°. The experiment required only half an hour.

With aluminium chloride (anhydrous) alone, allyl alcohol reacts very vigorously, giving very little allyl chloride and a large tar-like residue.

When calcium chloride and allyl alcohol are mixed, an additive compound is obtained, which, when heated at 80—90° in a stream of hydrogen chloride, gives a product boiling at 90—92°. This is probably diallyl ether, and contains only a trace of chloride.

Aschan's method (*loc. cit.*) for the formation of allyl chloride was tried, but although the yield on the ester actually used is 80 per cent., the reaction is extremely slow, and it is advantageous to prepare the alcohol and then use the method given first in this paper. An experiment was made by saturating allyl alcohol in the cold with hydrogen chloride in the presence of zinc chloride. The yield was not improved, however, and the reaction required a long period for completion.

One of us (C. F. W.) wishes to express his indebtedness to the Department of Scientific and Industrial Research for a grant which is enabling him to carry out these investigations.

One of us (S. C.) makes acknowledgment to the Royal Commissioners for the 1851 Exhibition for the grant of a research scholarship.

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CXLIX.—*Linolenic and Hexabromostearic Acids and some of their Derivatives.*

By SAMUEL COFFEY.

DURING an investigation on the oxidation of linseed oil it was desired to prepare pure linolic and linolenic acids just as they occur in the natural product.

It is doubtful whether pure linolic acid has ever been isolated. Hazura (*Monatsh.*, 1887, **8**, 260) prepared the corresponding tetrahydroxy-acid which was used by Goldsobel (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 904) in his researches on linolic acid, and Hazura and Grüssner (*Monatsh.*, 1888, **9**, 180) reduced the tetrabromide to a "linolic" acid which Rollet (*Zeitsch. physiol. Chem.*, 1909, **62**, 410) has shown to be a mixture of several isomerides. No method can be found in the literature of isolating this acid by means of its salts, and according to Lewkowitsch the only definitely crystalline salt is the zinc salt. Fernsteiner states that barium linolate, unlike the oleate, is soluble in dry benzene, but Lewkowitsch questions this.

In the case of linolenic acid, Erdmann and Bedford (*Ber.*, 1909, **42**, 1324) showed that the product of the action of zinc on linolenic acid hexabromide was a mixture of α- and β-linolenic acids, although only the α-modification occurs naturally. More recently, however, the former investigator (*Zeitsch. physiol. Chem.*, 1911, **74**, 179) claims to have prepared pure α-linolenic acid by fractional crystallisation from alcohol of the zinc salts of the liquid fatty acids of linseed oil. The zinc salt obtained, $(C_{18}H_{29}O_2)_2Zn,\frac{1}{2}ZnO$, melted at 72—73° and the yield was nearly theoretical, corresponding with 18 per cent. of linolenic acid in the liquid fatty acids.

Although ten separate attempts have been made by the author to repeat these experiments, in no case was he able to isolate pure zinc linolenate. The whole experimental evidence seems to show that the differences in solubility of zinc linolenate and zinc linolate are not nearly so marked as stated by Erdmann; in fact, the most soluble product is a mixture consisting principally of zinc linolate.

In the literature, the melting point of hexabromostearic acid is given as 177° (Hazura), 179° (Erdmann and Bedford), 180—181° (Hehner and Mitchell), and 181—182° (Rollet), but, as far as can be ascertained, the product has never been submitted to a careful purification by crystallisation.

Since α-linolenic acid has the constitution

$$C_2H_5\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$$

and gives on oxidation two hexahydroxy (linusic)-acids, it appeared not improbable that more than one hexabromo-acid would be produced. The results given in this paper, however, show no evidence of the presence of more than one hexabromostearic acid in the additive product.

EXPERIMENTAL.

Fractional Crystallisation of the Mixed Zinc Salts.

In most of the experiments the liquid fatty acids obtained from 100 grams of the original fatty acid mixture by freezing in light petroleum to −18° were converted into their zinc salts by trituration with basic zinc carbonate or oxide. The mixed zinc salts were then extracted once or several times with 250 c.c. of hot alcohol and the solution was allowed to crystallise by cooling. The most soluble part, crystallising out below 30°, usually had a melting point of 72—75°; it was redissolved and crystallised several times, the most soluble part only being taken. The final product (*a*) melted at 75·5—76·5°, crystallised in aggregates of needles, and appeared to be perfectly homogeneous; it gave a mixture of acids (d_4^{17} 0·899) which afforded only 14 per cent. of hexabromide. The salt contained only 10·5 per cent. of zinc (basic zinc linolenate requires 14·7 per cent.). The more sparingly soluble fractions gave a product (*b*) melting at 71—73°, which contained nearly 10 per cent. of linolenate and 10·5 per cent. of zinc; it appeared to be a mixture of constant melting point. The acids obtained from it had a density, d_4^{16} = 0·900.

In one case, the zinc salt in the original extract was crystallised nearly thirty times and the same fractions were obtained as before, namely, (*a*) most soluble, m. p. 75—76·5°, 9 grams, (*b*) m. p. 71—73°, 5 grams, from an original extract of 30 grams melting at 71—74°. It was also found that after 100 grams of zinc salts had been extracted three times with 300 c.c. of alcohol, the product extracted in a fourth operation still contained an appreciable quantity of linolenate, and even the most soluble salt from the mother-liquors proved to be a mixture.

On theoretical grounds Erdmann's results seem to be untrustworthy; he has extracted a mixture of compounds with alcohol, and claims to have isolated the *most soluble* component in a pure state by fractional crystallisation; which is certainly contrary to general practice. Since the above experiments show that the linolate is apparently very soluble, Erdmann's conclusions cannot be accepted.

With regard to the mixture of α- and β-acids obtained from the hexabromide, the author is able to confirm all the facts given by Erdmann and Bedford (*loc. cit.*).

Hexabromostearic Acid and its Salts.

Hexabromostearic acid was prepared from the mixed acids obtained from linseed oil by Erdmann and Bedford's method (*loc. cit.*). It was almost insoluble in hot or cold light petroleum (b. p. 100—140°), ether, or chloroform, but it was moderately soluble in hot benzene or acetic acid, from which it crystallised in small, colourless needles. In each case two crystallisations gave the pure hexabromostearic acid melting at 185° and even after seven or eight crystallisations this melting point was unchanged. The brown mother-liquor from the first crystallisation gave, on evaporation, a semi-solid "glue," from which it was possible to isolate a further quantity of the pure acid together with a few milligrams of a solid melting at 206—208° and a small amount of dark oil of low bromine content. Fractional crystallisation from alcohol, ethyl benzoate, phenol and ether, nitrobenzene, and tetrachloroethane also failed to alter the melting point of the acid. It was very sparingly soluble in alcohol and dissolution was only effected after prolonged boiling, during which some decomposition took place. The potassium and barium salts of this acid were prepared by Erdmann and Bedford (*loc. cit.*), and the sodium salt can be prepared by suspending the acid in sodium hydroxide solution, but these salts are so insoluble that it is impossible to recrystallise them.

Quinine monohexabromostearate was prepared by adding a hot benzene solution of the acid to a slight excess of quinine dissolved in the same solvent, and recrystallising the flocculent product. After three or four recrystallisations, the product melted constantly at 169° with decomposition, and the mother-liquors were found to contain nothing but the above salt and free quinine. The salt which had been crystallised eight times contained unchanged acid.

Quinine hexabromostearate is an ill-defined, crystalline compound; its melting point varies with the rate of heating, and the above result was obtained with a rise of 0·25° per second (Found : $C_{18}H_{30}O_2Br_6 = 70{\cdot}14$. $C_{18}H_{30}O_2Br_6,C_{20}H_{24}O_2N_2$ requires $C_{18}H_{30}O_2Br_6 = 70{\cdot}04$ per cent.).

Strychnine hexabromostearate was prepared by dissolving approximately equivalent quantities of the base and the acid in a mixture of 90 per cent. benzene and 10 per cent. absolute alcohol. The solution, when cooled, deposited a flocculent mass, which on recrystallisation darkened at 200° and melted fairly definitely and decomposed at 224—226°. After seven crystallisations, the melting point was unchanged and the acid prepared from the final product melted at 185°. The mother-liquors gave a small quantity of the salt and a little free strychnine. The strychnine salt is much more definite than the quinine compound, and crystallises in flat, microscopic rhombs (Found: $C_{18}H_{30}O_2Br_6 = 69{\cdot}4$ per cent. $C_{18}H_{30}O_2Br_6,C_{21}H_{22}O_2N_2$ requires $C_{18}H_{30}O_2Br_6 = 69{\cdot}4$ per cent.).

Morphine hexabromostearate was prepared from the acid and morphine dissolved in benzene containing a few units per cent. of alcohol. On cooling, the morphine salt was deposited and the mother-liquors were decanted. The salt, after three crystallisations, melted constantly at 181—182°. The acid prepared from the final product was identical with the original hexabromostearic acid.

Morphine hexabromostearate crystallises in aggregates of microscopic rhombs.

Narcotine hexabromostearate was obtained from a solution of the acid and narcotine in benzene. The salt, which rapidly crystallised on cooling, melted at 184°, and after seven crystallisations, the original acid was obtained from it.

An attempt was made to prepare the cinchonine salt, but this was a very indefinite product.

These experiments show that in all probability hexabromostearic acid obtained under these conditions is a homogeneous product.

In conclusion, the author wishes to express his indebtedness to the Department for Scientific and Industrial Research for a grant which enabled him to carry out part of this work, to Prof. F. S. Kipping, F.R.S., for his advice and encouragement, and to the Royal Commissioners for the 1851 Exhibition for the grant of a scholarship.

CHEMICAL DEPARTMENT.
UNIVERSITY COLLEGE, NOTTINGHAM [*Received, July 8th*, 1921.]

CL.—*Organo-derivatives of Thallium. Part II. Interaction of Thalliumdialkyl Hydroxides with Nitrophenols and Nitrocresols.*

By ARCHIBALD EDWIN GODDARD.

SINCE the thalliumdialkyl hydroxides bear a great resemblance to thallous compounds, and the latter to the derivatives of the alkali metals, a comparison has now been made between the behaviour of alkali hydroxides and thalliumdialkyl hydroxides towards the hydroxyl group in nitro-substituted phenol rings.

The hydroxides were obtained by treating thalliumdialkyl haloids with moist silver oxide. To these aqueous solutions was then added the calculated quantity of the nitrophenolic compound. The colours of the salts thus obtained resemble very closely those described for the alkaline-earth nitrophenoxides (Goddard, this vol., p. 1161), although the difference in solubility in passing from *o*- to *p*-nitrophenoxides is not so marked in the present case. It is again noticeable that the colour gradient between *meta*- and *para*-compounds is much greater than between *ortho*- and *meta*-. All thalliumdimethyl compounds have a more intense colour than the corresponding thalliumdiethyl compounds.

An interesting point with regard to the residual affinity of thallium is furnished by thalliumdimethyl *m*-nitrophenoxide, which was obtained both as a simple salt and also crystallised with 1 mol.

of *m*-nitrophenol. The colour of the latter was intense red, whilst the simple compound was yellowish-orange—this pointing to the fact that thallium requires an acid group for co-ordination (proved also by the fact that none of these compounds combines with ammonia), whereas the cobalt atom readily takes up alkaline groups.

Thalliumdiethyl 2 : 4-dinitrophenoxide is intermediate in colour between the *o*-nitrophenoxide and the picrate. The picramate, on the other hand, is very deep red, and its colour, in comparison with that of the pale yellow picrate, may be explained in the following way. The colour of the former may be due to the residual affinity existing between the amino-group and the thallium atom. Since thalliumdiethyl *p*-nitrophenoxide is only slightly coloured, the nitro-group in the 4-position probably has no effect on the colour. Applying this to the picrate, if the nitro-groups in positions 2 and 6 had any residual affinity, it would be exerted with equal and opposite force on the thallium atom, so that the colour here should be the same as that of the *p*-nitrophenoxide, this being in agreement with experimental results.

In the case of the thalliumdiethyl tolyloxides, the maximum colour is obtained when the methyl, the substituted hydroxyl, and the nitro-groups are in the positions 1 : 2 : 3; and as the latter two travel away from the methyl group to positions 1 : 3 : 4 the colour decreases. It is remarkable, however, that if the hydroxy- and nitro-groups are reversed, giving the 1 : 4 : 3-compound, the colour again increases, although not to the original intensity of the 1 : 2 : 3-compound.

When the hydroxyl and nitro-groups are in the *para*-position with respect to each other, as in thalliumdiethyl 6-nitro-*m*-tolyloxide, the methyl group being in the *ortho*-position to the nitro-group, the least coloured compound of the series is obtained. The 5-nitro-*o*-tolyloxide having the above groups in the *para*-position, but the methyl group *ortho* to the hydroxyl, exhibits more colour than the preceding compound, and has been obtained with 1 mol. of nitro-cresol of crystallisation.

The solubility of the thalliumdialkyl nitrophenoxides differs from that of the alkali compounds, since it decreases from *ortho*- to *para*-derivatives in both methyl and ethyl series. This applies also to the nitrotolyloxides, those having hydroxyl and nitro-groups in *ortho*-positions being less soluble than the compounds in which the same groups are in the *meta*- and *para*-positions.

Phenol itself also forms phenoxides, but these were found to be unstable on keeping, whilst the three cresols gave compounds which broke down on evaporating their aqueous solutions. *p*-Nitrosophenol forms a compound in the cold, but gentle warming is sufficient to destroy it.

EXPERIMENTAL.

Thalliumdimethyl o-*Nitrophenoxide*.—A solution of the hydroxide from 2 grams of thalliumdimethyl iodide in 50 c.c. of water and 0·77 gram of *o*-nitrophenol yielded a substance which, after three crystallisations from water, melted at 237° (1·2 grams) (Found: Tl=54·51; N=3·75. $C_8H_{10}O_3NTl$ requires Tl=54·77; N=3·76 per cent.). The salt crystallises in brick-red needles easily soluble in warm alcohol or pyridine, moderately soluble in acetone, chloroform or toluene, slightly soluble in ether or carbon tetrachloride, and insoluble in light petroleum.

Thalliumdiethyl o-*Nitrophenoxide*.—This was obtained by the interaction of 0·81 gram of *o*-nitrophenol and the thalliumdiethyl hydroxide derived from 2·0 grams of thalliumdiethyl bromide, the reaction being carried out in 50 c.c. of water (1 gram of pure product was obtained after crystallisation). The compound softened at 200° and melted with decomposition at 210° (Found: Tl=50·96; N=3·32. $C_{10}H_{14}O_3NTl$ requires Tl=50·93; N=3·49 per cent.). The salt crystallises in brilliant scarlet plates which are soluble in cold alcohol, ether, chloroform, acetone, or boiling toluene, and are insoluble in light petroleum.

Thalliumdimethyl m-*Nitrophenoxide*.—When the above quantities were used, two crops of crystals were obtained. (A) This crop crystallised in brilliant red cubes which softened at 150° and melted to a clear red liquid at 159° (0·3 gram) (Found: Tl=40·09; N=5·63. $C_8H_{10}O_3NTl,C_6H_5O_3N$ requires Tl=39·86; N=5·47 per cent.). The second deposit (B), which appeared on rapid cooling, was yellowish-orange plates (0·4 gram) which melted to a red liquid at 202°, the latter decomposing on boiling (Found: N=3·83 per cent.). This compound is therefore the normal salt and (A) may easily be transformed into it by washing with ether or alcohol. It is soluble in cold pyridine, acetone, or warm alcohol, moderately soluble in ether, toluene or chloroform, and insoluble in carbon tetrachloride or light petroleum.

Thalliumdiethyl m-*Nitrophenoxide*.—This compound was obtained in brownish-orange, oblong plates (0·85 gram) which darkened at 194° and melted at 196° (Found: Tl=50·58; N=3·51 per cent.). The compound was less soluble in the above-named solvents than the *ortho*-derivative.

Thalliumdimethyl p-*Nitrophenoxide*.—From the reaction, 1·0 gram of this compound was obtained, and it required four crystallisations from alcohol before it was sufficiently pure for analysis. It darkened at 273° and exploded violently at 275° (Found : Tl=54·70 per cent.). The salt crystallises in yellow plates which are easily soluble in cold pyridine, moderately soluble in alcohol or acetone, and insoluble in other organic solvents.

Thalliumdiethyl p-*Nitrophenoxide.*—This compound was obtained in lemon-yellow, rhomboidal plates (1·0 gram), darkening at 233° and melting at 238° (Found : Tl=50·85; N=3·46 per cent.). The salt is less soluble in water than the *ortho-* and *meta-*compounds, only moderately soluble in alcohol, acetone, or chloroform, less soluble in ether, and insoluble in boiling toluene or light petroleum.

Thalliumdiethyl 2 : 4-*Dinitrophenoxide.*—The thalliumdiethyl hydroxide from 2·0 grams of the corresponding bromide, when evaporated with 1·1 grams of 2 : 4-dinitrophenol, gave 1·5 grams of brownish-orange, crystalline plates melting at 174° (Found: Tl=45·79; N=6·32. $C_{10}H_{13}O_5N_2Tl$ requires Tl=45·77; N=6·29 per cent.). The salt is easily soluble in hot pyridine, moderately soluble in alcohol, acetone, or ether, slightly soluble in chloroform or toluene, and insoluble in carbon tetrachloride or light petroleum.

Thalliumdimethyl 4 : 6-*Dinitro-2-aminophenoxide.*—By interaction of the hydroxide from 1·5 grams of thalliumdimethyl iodide and 0·825 gram of picramic acid, 1·0 gram of product was obtained (Found: Tl=47·00; N=9·88. $C_8H_{10}O_5N_3Tl$ requires Tl=47·17; N=9·72 per cent.). The salt crystallises in small, deep reddish-violet plates darkening at 220° and melting with decomposition at 236°. It is easily soluble in alcohol, acetone, or pyridine, moderately soluble in ether, and insoluble in chloroform, carbon tetrachloride, toluene, or light petroleum.

Thalliumdiethyl 4 : 6-*Dinitro-2-aminophenoxide.*—To the hydroxide solution from 2·565 grams of thalliumdiethyl bromide, 1·49 grams of picramic acid were added. Evaporation gave 2·19 grams of product, darkening at 140° and melting with decomposition at 159° (Found: Tl=44·17; N=9·19. $C_{10}H_{14}O_5N_3Tl$ requires Tl=44·29; N=9·12 per cent.). The salt crystallises in small, carmine-red plates which have a metallic lustre and explode violently when moistened with fuming nitric acid. It is moderately soluble in alcohol, acetone, or pyridine, slightly soluble in chloroform, ether, or toluene, and insoluble in carbon tetrachloride or light petroleum.

Thalliumdiethyl 2 : 4 : 6-*Trinitrophenoxide.*—To the hydroxide solution from 2 grams of thalliumdiethyl bromide, 1·4 grams of picric acid were added; 0·99 gram of substance was obtained from the evaporated solution, the product darkening at 200° and melting with decomposition at 204° (Found : Tl=41·27; N=8·66. $C_{10}H_{12}O_7N_3Tl$ requires Tl=41·58; N=8·56 per cent.). The salt crystallises in golden-yellow, oblong plates, very soluble in water or cold alcohol, ether, chloroform, or acetone, moderately sol in boiling toluene, and insoluble in light petroleum.

Thalliumdimethyl 3-*Nitro*-o-*tolyloxide.*—By the interaction of the hydroxide from 2 grams of thalliumdimethyl iodide and 0·765 gram of 3-nitro-*o*-cresol, deep red, crystalline plates (0·99 gram) having a brown reflex were obtained. These melted at 186·5° to a deep red liquid (Found: Tl=52·24; N=3·81. $C_9H_{12}O_3NTl$ requires Tl=52·77; N=3·62 per cent.). The salt is readily soluble in cold pyridine, warm alcohol, acetone, ether, toluene, or chloroform, moderately soluble in carbon tetrachloride, and slightly soluble in light petroleum. The colour of all these solutions is red, dilution not completely destroying the red tone.

Thalliumdiethyl 3-*Nitro*-o-*tolyloxide.*—When the hydroxide from 2·7 grams of thalliumdiethyl bromide reacted with 1·2 grams of the nitrocresol, 1·32 grams of product were obtained on evaporation (m. p. 190—191°) (Found: Tl=49·18; N=3·68. $C_{11}H_{16}O_3NTl$ requires Tl=49·19; N=3·38 per cent). The salt crystallises in deep red plates having a green reflex and is easily soluble in cold alcohol, ether, chloroform, pyridine, or boiling toluene, moderately soluble in water or hot carbon tetrachloride, and slightly soluble in light petroleum.

Thalliumdiethyl 4-*Nitro*-m-*tolyloxide.*—When the same quantities as for the above preparation were used, 0·97 gram of pale red plates was obtained, which darkened at 220° and exploded violently at 228° (Found: Tl=48·80; N=3·49 per cent.). The salt is moderately soluble in alcohol, ether, or pyridine, slightly soluble in toluene, chloroform, or carbon tetrachloride, and insoluble in light petroleum.

Thalliumdiethyl 3-*Nitro*-p-*tolyloxide.*—This was prepared from 2·0 grams of thalliumdiethyl bromide and 0·89 gram of nitrocresol, when 1·13 grams of product, softening at 200° and melting at 206°, were obtained (Found: Tl=49·08; N=3·30 per cent.). The salt crystallises in small, ruby red, rhomboidal plates having a green lustre, is easily soluble in hot pyridine, moderately soluble in chloroform or toluene, slightly soluble in alcohol ether, acetone, or carbon tetrachloride, and insoluble in light petroleum.

Thalliumdiethyl 6-*Nitro*-m-*tolyloxide.*—With the above quantities, 1·26 grams of pure substance were isolated, darkening at 210° and melting with decomposition at 216·5° (Found: Tl=49·33; N=3·63 per cent.). The salt crystallises in small, lemon-yellow plates which are easily soluble in cold pyridine, hot alcohol, or acetone, slightly soluble in ether or chloroform, and insoluble in carbon tetrachloride, toluene, or light petroleum.

Thalliumdiethyl 5-*Nitro*-o-*tolyloxide.*—The hydroxide from 2·12 grams of bromide and 0·94 gram of nitrocresol yielded 0·85 gram of product softening at 165° and melting to a red liquid at 181·5° (Found: Tl=36·11; N=4·45. $C_{11}H_{16}O_3NTl,C_7H_7O_3N$ requires Tl=35·91; N=4·93 per cent.). The salt crystallises in brownish-yellow plates which are easily soluble in cold water, pyridine, warm alcohol, or acetone, moderately soluble in ether or chloroform, slightly soluble in toluene, and insoluble in carbon tetrachloride or light petroleum.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

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[*Received, July 5th,* 1921.]

CLI.—*The Formation and Stability of* spiro-*Compounds. Part VI. New Derivatives of* cyclo*Propane and* cyclo*Hexane*spirocyclo*propane.*

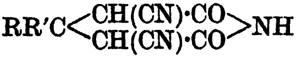
By STANLEY FRANCIS BIRCH, WILLIAM HENRY GOUGH, and GEORGE ARMAND ROBERT KON.

THE results recently attained from a study of dialkyl- and *spirocyclo*propane compounds made it appear desirable to extend our knowledge of the methods by which such compounds can be obtained. Up to the present they have usually been prepared in these laboratories by the action of hydrolysing agents on the esters of the bromo-substituted glutaric acids (compare Beesley, Ingold, and Thorpe, T., 1915, **107**, 1080; Becker and Thorpe, T., 1920, **117**, 1579; Perkin and Thorpe, T., 1899, **75**, 48) and although a fair variety of starting material was thus available, the products consisted of a few types only.

It was therefore decided to search for new sources of such compounds and also to endeavour to increase the variety of the compounds obtainable, with the object of comparing their stability.

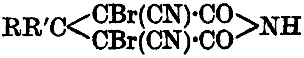
An examination of the literature revealed a possible source of *cyclo*propane derivatives in the bridged piperidine compounds described by Guareschi (*Mem. R. Accad. Sci. Torino*, 1901, **50**, 235; *Atti R. Accad. Sci. Torino*, 1910–1911, **46**, 662; Guareschi and Grande, *ibid.*, 1898–1899, **34**, 924). These compounds are formed in almost quantitative yield when the imides of the general type

(I), obtained by the condensation of ketones with ethyl cyanoacetate and ammonia, are brominated and the resulting dibromo-compounds (II) are subjected to the action of heat, or treated with some agent capable of eliminating bromine, such as formic acid or even alcohol. Formula III was assigned by Guareschi to these compounds,



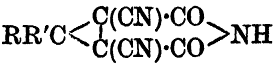
$RR'C<\begin{matrix}CH(CN)\cdot CO\\ CH(CN)\cdot CO\end{matrix}>NH$

(I.)



$RR'C<\begin{matrix}CBr(CN)\cdot CO\\ CBr(CN)\cdot CO\end{matrix}>NH$

(II.)



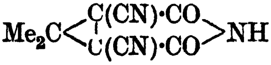
$RR'C<\begin{matrix}C(CN)\cdot CO\\ |\\ C(CN)\cdot CO\end{matrix}>NH$

(III.),

although no proofs of its correctness, beyond the elementary analysis, were supplied by him.

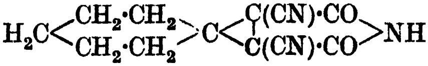
At first it appeared unlikely that this constitution could be correct owing to the ease with which the " bridging " takes place, this being seldom observed in reactions leading to *cyclo*propane compounds. It was therefore decided to investigate the matter further and, should Guareschi's formula prove correct, to endeavour to utilise these compounds as a source of *cyclo*propane derivatives, more particularly of those which are not obtainable by the methods already in use.

Two typical examples were chosen, namely, the dimethyl compound (IV) and the *cyclo*hexane compound (V), which should, if Guareschi's formula is correct, be convertible respectively into caronic acid (VI) and *cyclo*hexane*spirocyclo*propanedicarboxylic acid (VII) or their derivatives :



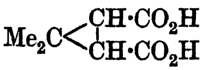
$Me_2C<\begin{matrix}C(CN)\cdot CO\\ |\\ C(CN)\cdot CO\end{matrix}>NH$

(IV.)



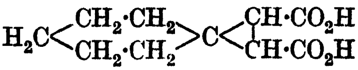
$H_2C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}C(CN)\cdot CO\\ |\\ C(CN)\cdot CO\end{matrix}>NH$

(V.)



$Me_2C<\begin{matrix}CH\cdot CO_2H\\ |\\ CH\cdot CO_2H\end{matrix}$

(VI.)



$H_2C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH\cdot CO_2H\\ |\\ CH\cdot CO_2H\end{matrix}$

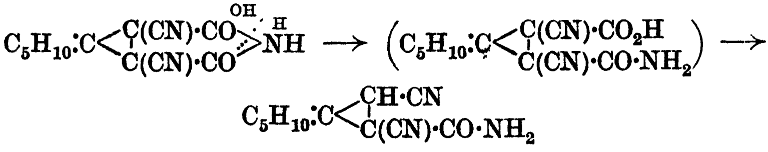
(VII.)

The latter two acids have already been studied in detail (Beesley, Ingold, and Thorpe, *loc. cit.*), especially with regard to their stability. It was clearly shown that the *cyclo*hexane-compound is the more readily formed and the more stable, which points to the influence of the *cyclo*hexane ring in conferring stability on a *cyclo*propane ring having a carbon atom in common with it.

It was most important definitely to establish the constitution of Guareschi's bridged imides, but the problem proved to be one of considerable difficulty owing, particularly, to the large number of products which could be obtained from these compounds by the action of various reagents; ultimately, however, it was possible to demonstrate the correctness of the general constitution (III) assigned to them.

It was soon discovered that the use of acid hydrolysing agents caused deep-seated changes, but regulated hydrolysis with alkali led to the formation of a variety of products according to the conditions of the experiment.

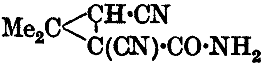
It was found that the *cyclo*hexane compound (V) was somewhat more readily hydrolysed than the dimethyl compound (IV). If it is boiled for a few minutes with one molecular proportion of 10 per cent. aqueous potassium hydroxide, the imino-ring is broken and at the same time a molecule of carbon dioxide is eliminated, the amide (VIII) being obtained in almost quantitative yield:



$$C_5H_{10}{:}C<\begin{matrix}C(CN)\cdot \overset{OH}{CO}\\ C(CN)\cdot CO\end{matrix}>\overset{H}{N}H \longrightarrow \left(C_5H_{10}{:}C<\begin{matrix}C(CN)\cdot CO_2H\\ C(CN)\cdot CO\cdot NH_2\end{matrix}\right) \longrightarrow C_5H_{10}{:}C<\begin{matrix}CH\cdot CN\\ C(CN)\cdot CO\cdot NH_2\end{matrix}$$

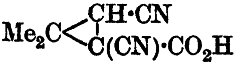
(VIII.)

An exactly analogous compound (IX) is produced from the imide (IV), except that some of the original substance is always recovered unchanged.



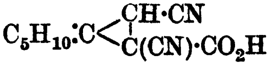
$$Me_2C<\begin{matrix}CH\cdot CN\\ C(CN)\cdot CO\cdot NH_2\end{matrix}$$

(IX.)



$$Me_2C<\begin{matrix}CH\cdot CN\\ C(CN)\cdot CO_2H\end{matrix}$$

(X.)



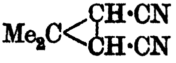
$$C_5H_{10}{:}C<\begin{matrix}CH\cdot CN\\ C(CN)\cdot CO_2H\end{matrix}$$

(XI.)

On further hydrolysis with alkali, these compounds undergo fission (see below); it is, however, possible to obtain from them the acids (X) and (XI) by the action of nitrous acid. The yields are not good, but the unchanged material can be recovered.

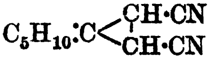
The dicyano-acids (X) and (XI) can also be prepared directly from the imides by acting on the latter with two molecular proportions of potassium hydroxide in dilute solution, but the best conditions are difficult to establish, and the use of nitrous acid is preferable.

Although the amides are not affected by heating with water under pressure at 180°, the corresponding acids readily lose carbon dioxide under these conditions and are converted into the dinitriles (XII) and (XIII), from which the dicarboxylic acids (VI and VII) can be obtained by digestion with alcoholic potassium hydroxide.



$$Me_2C<\begin{matrix}CH\cdot CN\\ CH\cdot CN\end{matrix}$$

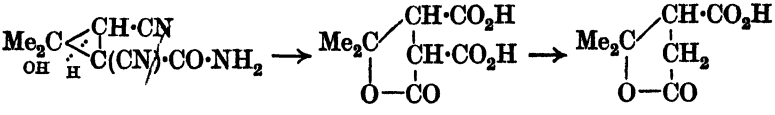
(XII.)



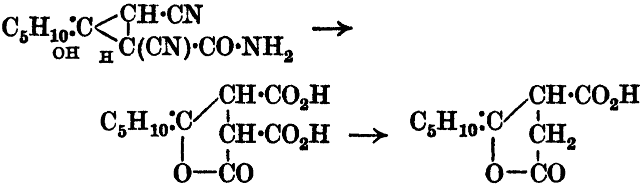
$$C_5H_{10}{:}C<\begin{matrix}CH\cdot CN\\ CH\cdot CN\end{matrix}$$

(XIII.)

It is noteworthy that no fission occurs, although the action of potassium hydroxide on the amides (VIII) and (IX), no doubt owing to the presence of two quaternary carbon atoms, leads rapidly to the splitting of the *cyclo*propane ring with the formation of the lactonic acids (XIV) and (XVI):



(XIV.) (XV.)



(XVI.) (XVII.)

At first the nature of these fission products was not clear, but it was found that they readily lose a molecule of carbon dioxide on heating, or on boiling with dilute sulphuric acid.

In the case of the dimethyl compound the product was the well-known terebic acid (XV), so that the fission of the original amide must have taken place in the manner indicated, that is, between the two quaternary carbon atoms.

The ready fission of the amides on hydrolysis is quite analogous to the behaviour of the hydroxy-*spiro*-acid recorded by Beesley, Ingold, and Thorpe (*loc. cit.*). This substance undergoes fission between the two quaternary carbon atoms on heating with water under pressure, whereas the unhydroxylated *spiro*-acid is quite stable under the same conditions.

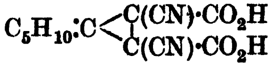
In the reactions described above there is little difference between the behaviour of the dimethyl- and the *cyclo*hexane-compounds and no inferences can be drawn as to their relative stability.

Evidence bearing on the question is, however, readily obtained on studying the behaviour of the two bridged imides on treatment with three or more molecular proportions of alkali.

In the first place, if these two compounds are subjected to the action of very concentrated alkali at a high temperature, the main product obtained from the *cyclo*hexane compound is the lactonic acid (XVI), but an appreciable amount of the *spiro*-acid (VIII) is also formed. Not a trace of caronic acid (VI) could, however, be isolated in similar experiments with the dimethyl compound and it must be concluded that here the *cyclo*propane ring is too unstable to survive the experimental conditions.

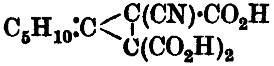
Such drastic treatment is not, however, necessary to demonstrate the difference of stability between the two series of compounds.

The most striking evidence on this point is afforded by the hydrolysis of the original imides by means of three molecular proportions of potassium hydroxide in aqueous solution. Under these conditions the *cyclo*hexane compound yields the acid (XVIII) almost quantitatively; if the boiling is very prolonged, the substance (XIX) is also produced.



$$C_5H_{10}:C<\begin{array}{l}C(CN)\cdot CO_2H\\ |\\ C(CN)\cdot CO_2H\end{array}$$

(XVIII.)

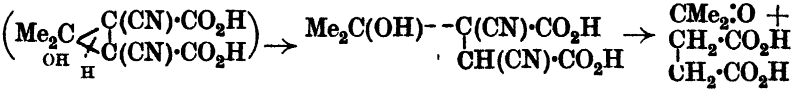


$$C_5H_{10}:C<\begin{array}{l}C(CN)\cdot CO_2H\\ |\\ C(CO_2H)_2\end{array}$$

(XIX.)

It is interesting to note, in passing, that if sufficient alkali (3 mols. is used in the hydrolysis, carbon dioxide is not eliminated and substances with three quaternary carbon atoms are produced; otherwise the amide (VIII) or its products of hydrolysis are formed in greater or smaller amount.

When the amide (IV) is hydrolysed in the same way, an analogous acid is obtained in fair yield, but this acid has the expected composition with the addition of one molecule of water. The constitution of this substance (XX) follows clearly from the fact that on boiling with dilute sulphuric acid it is rapidly and quantitatively split into acetone and succinic acid, the latter being produced by the hydrolysis of the dicyanosuccinic acid first formed:



$$\left(Me_2C\begin{array}{l}\nearrow C(CN)\cdot CO_2H\\ \ \ \ \ |\\ \underset{OH}{}\ \underset{H}{\nwarrow} C(CN)\cdot CO_2H\end{array}\right)\rightarrow Me_2C(OH)\text{--}\begin{array}{l}C(CN)\cdot CO_2H\\ |\\ CH(CN)\cdot CO_2H\end{array}\rightarrow \begin{array}{l}CMe_2:O\ +\\ CH_2\cdot CO_2H\\ |\\ CH_2\cdot CO_2H\end{array}$$

(XX.)

It is certainly remarkable that the acid (XX), which is a γ-hydroxy-acid, does not pass into a lactone under the experimental conditions used;* but its behaviour on hydrolysis is, we think, sufficient proof of its constitution. That the substance represented by the formula (XVIII) is not the lactone of a hydroxy-acid similar to the acid (XX) is clearly proved by the fact that it forms an anhydride from which the original acid is readily regenerated.

It will thus be seen that the results described in the present paper strongly support the views expressed by Beesley, Ingold, and Thorpe regarding the stability of *spirocyclo*propane compounds.

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* For other examples of γ-hydroxy-acids not forming lactones, see Kiliani and Loeffler, *Ber.*, 1905, **38**, 3624; Kiliani and Matthes, *ibid.*, 1907, **40**, 1238.

EXPERIMENTAL.

Preparation of Guareschi's Bridged Imides (IV and V).

The method used was a modification of that described by Guareschi (*Atti R. Accad. Sci. Torino*, 1910–1911, **46**, 662).

One-tenth of a gram-molecule of the finely powdered dicyano-imide (obtained by Guareschi's method; compare Kon and Thorpe, T., 1919, **115**, 686; Kon, this vol., 818) is suspended in 160 c.c. of water and 32 grams of bromine are gradually added with vigorous shaking. Hydrogen bromide is evolved and the liquid finally assumes a permanent yellow tinge, due to excess of bromine. The suspension of the dibromo-compound is treated with 160 c.c. of formic acid (80 per cent.) and the mixture slowly heated to boiling with constant stirring to prevent frothing; it is finally allowed to boil for a few minutes. On cooling, the bridged compound separates out; it is collected, and a further small amount can be recovered by diluting the mother-liquors with water.

The dimethyl compound (IV) was found to melt at 242° (Found: C=56·99; H=3·81; N=22·41. Calc., C=57·11; H=3·73; N=22·22 per cent.) and the *cyclo*hexane compound (V) at 233° (Found: N=18·54. Calc., N=18·38 per cent.).

2 : 3-*Dicyano*-1 : 1-*dimethyl*cyclo*propane*-2-*carboxylamide* (IX).

The imide (IV) was boiled with 10 per cent. aqueous potassium hydroxide (1 mol.) for five minutes and then cooled in ice. The amide crystallised out and was collected, further quantities being recovered by extracting the mother-liquors with ether. On acidifying the mother-liquors, some of the imide was precipitated; it is usually preferable to repeat the heating once or twice before recovering the unchanged material.

The *amide* obtained in this way crystallises from hot water,* dilute alcohol, or benzene in long, flattened needles melting at 163·5° (Found: C=58·77; H=5·73; N=25·93. $C_8H_9ON_3$ requires C=58·85; H=5·76; N=25·74 per cent.).

2 : 3-*Dicyano*-1 : 1-*dimethyl*cyclo*propane*-2-*carboxylic Acid* (X).

The amide (5 grams) was dissolved in cold concentrated sulphuric acid (100 c.c.), the mixture cooled in ice, and a saturated solution of sodium nitrite in water added drop by drop with stirring until the mixture became nearly solid. It was allowed to remain for an hour, poured into water, and the aqueous fluid repeatedly with ether, which dissolved both the new acid and the anged material; the acid was then separated from the latter ng the extract with a solution of sodium carbonate and ed from the alkaline solution by acidifying and extracting her in the usual way. It should be remembered, however, th the acid and its amide are somewhat sparingly soluble

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* This solvent is not to be recommended, as it tends to hydrolyse the amide.

slowly crystallises from water in large, transparent, laminæ melting at 168—169°. It is almost insoluble in oroform, or light petroleum, and does not decolorise ganate in the cold (Found: C=58·83; H=5·10; N O_2N_2 requires C=58·50; H=4·94; N=17·05 per cen

obtained by boiling the imide (IV) with 7·5 * per cent. aq ium hydroxide (2 mols.) for about one hour. The liquid gr umes a purplish-brown colour with a green fluorescence an mmonia is evol[illegible] After being cooled, it is extracted with ether to remove a[illegible]de produced (by partial hydrolysis) and acidified, the col[illegible]nging to deep violet; a 20 per cent. yield of the acid can [illegible] tained by extracting the solution with ether.

It was thought desirable to investigate the nature of the by-products formed in this reaction, and therefore the mother-liquors from several experiments were combined and kept for about three weeks. At the end of that time a considerable amount of crystalline solid had separated, which was collected and recrystallised from water. It was found to melt with vigorous decomposition at 195—196° and t[illegible] of the acid XX (see below).

The mo[illegible]r from this substance was neutralised with ammonia, [illegible]ed to dryness, ground with concentrated hydrochloric aci[illegible]lowed to evaporate to dryness in an exhausted desiccator [illegible]ium hydroxide. The solid was extracted with acetone an[illegible]sidue obtained on removing the solvent spread on porous [illegible], and then crystallised from water with the use of animal [illegible]. The crystals which separated consisted of a mixture o[illegible]ompounds, which were separated by boiling chloroform[illegible]

The sub[illegible]oluble in chloroform was non-nitrogenous and crystallise[illegible]ater in small, colourless prisms melting at 173—174°. It [illegible]ved to consist of terebic acid (XV) by direct compariso[illegible] melting point) with a specimen of that substance.

The sec[illegible]tance contained nitrogen and crystallised from

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Th[illegible] per cent. potassium hydroxide is to be preferred.

water in fine, long needles melting not very sharply at 234—[illegible] with slight decomposition (Found : C=53·24; H=5·58. C_8H_{10}[illegible] requires C=53·31; H=5·60 per cent.). This substance is pro[illegible] represented by the formula $OH·CMe_2·CH(CN)·CH(CN)·CO_2H$[illegible]

Nitrile of 1 : 1 *Dimethyl*cyclo*propane*-2 : 3-*dicarboxylic Aci*[illegible]

Four grams of the acid (X) were heated with a little wa[illegible] sealed tube for an hour at 180—200°, when a light yello[illegible] found floating on the surface of the water. The product[illegible] such experiments were combined, the oil taken up i[illegible] ethereal solution carefully washed, first with aque[illegible]m hydroxide and then with water, dried, and eva[illegible]

The residual oil representing a yield of 5[illegible]the theoretical, boiled at 158°/12 mm. and solidifi[illegible]ome time. On crystallising the solid from eth[illegible] petroleum (b. p. 30—40°), it separated in long, flatte[illegible]es melting at 50° (Found : N=23·28. [illegible]N_2 requires N=[illegible]32 per cent.).

The alkaline washing[redacted]ed above were found to contain a very small amount of a e of acids (probably the original acid with caronic acid) *imide* melting, after purification, at 163·5°, and doubtless consisting of *caronimide* (Found : N=10·40 $C_7H_9O_2N$ requires N=10·07 per cent.).

cis- *and* trans-1 : 1-*Dimethyl*cyclo*propane*-2 : 3-*dicarboxylic Acids* (*Caronic Acids*) (VI).

A solution of the dinitrile (2 grams) in 25[redacted]ent. aqueous potassium hydroxide (20 c.c.) and warm alcoho led for four hours, the alcohol then allowed to evaporate, a iquid, after being cooled, extracted with ether to remove an ged nitrile, then strongly acidified, and again extracted wit The second extract, on evaporation, yielded 2·2 grams of ixed acids. The separation into *cis*- and *trans*-forms was car s described by Perkin and Thorpe (*loc. cit.*), 1·3 grams of the d 0·5 gram of the *cis*-acid being obtained.

The former separated from water in feathery nd melted at 213° (Found : C=52·91; H=6·38. Calc., ; H=6·39 per cent. Titration with 0·0264*N*-barium h Found, 24·4 c.c. Calc., 24·3 c.c.).

The *cis*-acid separated from water in plates me decomposing at 174—175° (Found : C=52·93; H=6·40 .).

There is some evidence to show that the use o ncentrated potassium hydroxide favours the formation of th dification.

[illegible]tone of β-*Hydroxy*-β-*methylbutane*-γδδ-*tricarboxylic Acid* (XIV).

The amide (3·8 grams) was dissolved in aqueous potassium hydroxide (6 grams in 45 c.c. of water) and the solution boiled until ammonia ceased to be given off (three to four hours). The solution was cooled, acidified, and repeatedly extracted with pure ether. On removing the ether, about 2 grams of a solid acid were obtained. The purification of this substance presented very considerable difficulties, as it proved to be very soluble in water. It separated from a small quantity of water in large, colourless prisms melting and decomposing at 157° (Found: C=47·72; H=5·08. $C_8H_{10}O_6$ requires C=47·50; H=5·00 per cent.).

The *silver* salt is very soluble in water and was not analysed for this reason, but the constitution of the substance follows from its ready conversion into terebic acid, as well as its similarity to the *cyclo*hexane compound (see p. 1326).

Lactone of β-*Hydroxy*-β-*methylbutane*-γδ-*dicarboxylic Acid* (*Terebic Acid*) (XV).

When the acid described above is warmed for a short time with sulphuric acid (25 per cent.), it readily loses 1 molecule of carbon dioxide and is converted into terebic acid. The change appears to take place even on boiling with water. The boiling was usually continued until no further evolution of gas occurred; the liquid on cooling deposited spherical clusters of prisms which, after one crystallisation from water, melted sharply at 174° and answered the usual tests for terebic acid (Perkin and Thorpe, *loc. cit.*) (Found: C=53·01; H=6·49. Calc., C=53·12; H=6·39 per cent.).

αβ-*Dicyano*-γ-*hydroxy*-γ-*methylbutane*-αβ-*dicarboxylic Acid* (XX).

The imide (IV) was dissolved in 10 per cent. aqueous potassium hydroxide (3[illegible]nd the solution boiled for half an hour. The purple fluore[illegible]ution was cooled and acidified, when the above acid slowly [illegible]d, the yield being about 70 per cent. of the theoretical.* [illegible]acid slowly crystallises from water, forming th[illegible]rhombic plates melting and decomposing at 19[illegible]: C=47·67; H=4·46; N=12·45. $C_9H_{10}O_5N_2$ req[illegible] H=4·47; N=12·39 per cent.). It is very sparingly s[illegible]ether, but dissolves readily in hot water. The *silver* salt a[illegible]be very soluble in water and is not precipitated by alcohol. [illegible]

The aci[illegible]be titrated satisfactorily (Found: 13·5 c.c. of

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* The m[illegible]ors appear to contain more of the same substance.

$N/10NaOH$. Calc., 14·3 c.c.), although the result clearly indic[illegible] that it is dibasic.

Five grams of the acid were boiled with 50 c.c. of 50 per cent. sulphuric acid. The flask was provided with an air condenser, the end of which was bent over and dipped into a solution of semicarbazide acetate. Almost as soon as the liquid began to boil a precipitate was formed in this solution and gradually increased, while the liquid in the flask evolved a quantity of carbon dioxide. The action appeared to be over in less than an hour, the sulphuric acid solution remaining almost colourless. On cooling, the characteristic crystals of succinic acid separated from this solution, a small additional amount being recovered by means of ether. The yield was nearly quantitative; after two crystallisations from water, the acid melted at 185° and was identified in the usual way (Found: C=40·76; H=5·42. Calc., C=40·70; H=5·08 per cent.).

The semicarbazone precipitated melted at 187° and had the characteristic appearance of acetonesemicarbazone; it did not depress the melting point of a genuine specimen of that substance (Found: N=36·85. Calc., N=36·48 per cent.).

Action of Concentrated Potassium Hydroxide on the Imide IV.

Forty-eight grams of potassium hydroxide were heated with 12 c.c. of water until dissolved and 4 grams of the imide were gradually added. Each addition caused much frothing, and the mixture was finally heated for a few minutes until this subsided. When cold, the mass was dissolved in a small quantity of water, the solution extracted with ether to remove any neutral substances formed, strongly acidified, and again extracted eight times with an equal bulk of ether. The ethereal extract gave on evaporation a very small amount of an oil which solidified when kept in a vacuum. It was very soluble in water, and obviously consisted of the acid XIV (see above, p. 1323), but it could not be induced [redacted] allise from its solution. It was therefore boiled with a little ent. aqueous sulphuric acid, when the characteristic crystal ic acid were readily obtained on cooling the solution. The lted at 174°, and was identified by direct comparison with at substance. In spite of a diligent search, no t s-caronic acid could be isolated from the pro ve reaction.

cyclo*Hexane*spiro-2 : 3-*dicyano*cyclo*propane-2-c* *ide* (VIII).

This was obtained from the *spiro*-imide (he method described for the dimethyl compound (p. 1320 parates in almost quantitative yield on cooling; extraction with ether is not necessary.

The compound crystallises best from dilute alcohol or benzene, and is obtained in fine, glistening plates or sometimes in colourless, felted needles. It melts at 141° (Found: C=65·34; H=6·56; N=20·94. $C_{11}H_{13}ON_3$ requires C=65·00; H=6·45; N=20·67 per cent.).

cyclo*Hexane*spiro-2 : 3-*dicyano*cyclo*propane-2-carboxylic Acid* (XI).

The acid is best obtained from the above amide by means of nitrous acid, in the same way as the corresponding dimethyl compound (p. 1320). The yield is about 30 per cent. of the theoretical, the unchanged amide being recovered.

The acid can also be prepared by the direct hydrolysis of the imide (V) with potassium hydroxide (2 mols.). It is necessary, in this case, to use an alcoholic solution of potassium hydroxide, otherwise the amide melting at 141° will tend to separate, being quite insoluble in aqueous alkali. This method of preparation is not to be recommended, as the yield is only 20 per cent. of the theoretical, and a considerable quantity of the lactonic acid (XVI) is produced as the result of hydrolytic fission.

The dicyano-acid obtained by either method forms colourless prisms melting at 159°. It crystallises best when it is dissolved in a small quantity of water and an equal volume of concentrated hydrochloric acid is added to the solution (Found: C=65·03; H=5·99; N=13·73. $C_{11}H_{12}O_2N_2$ requires C=64·69; H=5·93; N=13·72 per cent. Titration with 0·0264*N*-barium hydroxide: Found: 3·97 c.c. Calc., 3·96 c.c.).

The Nitrile of cyclo*Hexane*spirocyclo*propane-2 : 3-dicarboxylic Acid.*

On heating the above dicyano-acid with water in a sealed tube in the way described for the dimethyl compound, the nitrile was obtained as a semi-solid mass. It solidified completely when treated with sodium hydrogen carbonate solution, which removed the unchanged acid, and was purified by crystallisation from dilute alcohol. It separated in lustrous, colourless plates melting at 86°. The yield was about 45 per cent. of the theoretical (Found: N=17·75. $C_{10}H_{12}N_2$ requires N=17·49 per cent.).

cyclo*Hexane*spirocyclo*propane-2 : 3-dicarboxylic Acid* (VII).

A quantitative yield of this acid was obtained when the above nitrile was hydrolysed under the condition described for the preparation of *cis*- and *trans*-caronic acids (see p. 1322).

Only a small quantity of the *cis*-modification appeared to be ormed, and this was not isolated in a pure state (m. p. 195—196° with decomp.).

The *trans*-acid was readily obtained and corresponded in all its properties with the description given by Beesley, Ingold, and Thorpe (*loc. cit.*); it melted at 238°, and gave an anilide melting at 291° (these authors give 237° and 292° respectively); the identity of these compounds was further confirmed by direct comparison with the original specimens (mixed melting points).

γ-*Lactone of* 1-*Hydroxy*cyclo*hexylethane*-αββ-*tricarboxylic Acid* (XVI).

The amide (4·5 grams) was boiled with 45 c.c. of 15 per cent. aqueous potassium hydroxide until ammonia ceased to be evolved (four hours). On acidifying the cooled solution and allowing it to remain over-night, the new acid separated in characteristic spherical aggregates of buff-coloured crystals; a further quantity was obtained on extracting the mother-liquors with ether, the total yield being about 3 grams.

The acid crystallises best from water with the addition of hydrochloric acid. It does not melt sharply, probably because it tends to lose carbon dioxide on boiling with water; usually it melts and decomposes at 183—184°, although melting points up to 191° have been observed (Found: C=54·66; H=6·12. $C_{11}H_{14}O_6$ requires C=54·53; H=5·82 per cent.).

The proof of its structure was obtained by boiling a solution of the acid in dilute ammonia until neutral and adding an excess of silver nitrate solution, when the *silver* salt of the corresponding tribasic hydroxy-acid separated (Found: Ag=55·94. $C_{11}H_{14}O_7Ag_3$ requires Ag=55·72 per cent.).

The acid is not affected by boiling with acetyl chloride and is therefore probably the *trans*-isomeride.*

On heating to a temperature just above its melting point, the acid decomposes vigorously and a molecule of carbon dioxide is eliminated without any charring. The product consists of the lactonic acid described below.

γ-*Lactone of* 1-*Hydroxy*cyclo*hexylethane*-αβ-*dicarboxylic Acid* (XVII).

The lactonic acid XVI (6 grams) was boiled with 20 per cent. sulphuric acid (200 c.c.) until all was dissolved and the evolution of carbon dioxide had ceased. On cooling, a new acid was obtained in good yield; this was repeatedly crystallised from water and separated in plates melting at 184—185°. It is almost insoluble in cold water (Found: C=60·30; H=7·05. $C_{10}H_{14}O_4$ requires C=60·57; H=7·12 per cent.).

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* An anilide melting at 278° was prepared from this acid by heating it with aniline, but the quantity was not sufficient for analysis.

The *silver* salt of the lactonic acid is readily obtained in the usual way (Found: Ag=35·64. $C_{10}H_{13}O_4Ag$ requires Ag=35·38 per cent.).

The *silver* salt of the dibasic hydroxy-acid was prepared by dissolving the lactonic acid in an excess of boiling *N*/10-sodium hydroxide; the excess of alkali was neutralised with nitric acid and an excess of silver nitrate added (Found: Ag=50·63. $C_{10}H_{14}O_5Ag_2$ requires Ag=50·19 per cent.).

The lactonic acid is stable to permanganate. If it is heated to boiling in a test-tube for a few moments and then cooled, the residue, dissolved in a little aqueous sodium hydrogen carbonate, instantly reduces permanganate. This property is also characteristic of the similarly constituted terebic acid (Perkin and Thorpe, *loc. cit.*).

The acid gives a characteristic *anilide* when heated with aniline at 200° for a short time, but the compound appears to be abnormal, being formed from equimolecular proportions of the acid and the base by the elimination of one molecule of water and one of carbon dioxide. It crystallises from dilute alcohol in iridescent plates melting at 113° (Found: C=77·85; H=8·30; N=6·20. $C_{15}H_{19}ON$ requires C=78·58; H=8·33; N=6·11 per cent.).

cyclo*Hexane*spiro-2 : 3-*dicyano*cyclo*propane*-2 : 3-*dicarboxylic Acid* (XVIII).

A solution of the imide V in 10 per cent. aqueous potassium hydroxide (3 mols.) was boiled for thirty to forty minutes, and then cooled and acidified, when the above acid was deposited in almost quantitative yield. It crystallises from dilute alcohol in small plates melting and decomposing at 207° (Found: C=58·20; H=5·03; N=11·32. $C_{12}H_{12}O_4N_2$ requires C=58·07; H=4·88; N=11·28 per cent.). The acid, although evidently dibasic, did not give satisfactory figures on titration.

The acid was heated just above its melting point until the evolution of vapour ceased (twenty minutes). The residue set to a stiff gum on cooling; it was taken up in ether, the solution washed with sodium carbonate solution, dried, and evaporated, the solid residue being crystallised from benzene. It separated in distinctly coloured, microscopic crystals melting at 99°, and proved to be the *anhydride* of the above acid, as it was transformed into the latter on hydration (Found: N=12·30. $C_{12}H_{10}O_8N_2$ requires N=12·17 per cent.).

cyclo*Hexane*spiro-2-*cyano*cyclo*propane*-2 : 3 : 3-*tricarboxylic Acid* (XIX).

If either the imide (V) or the dicyano-dicarboxylic acid (XVIII) is hydrolysed with an excess of potassium hydroxide for some hours, the potassium hydrogen salt of the above acid separates on acidifying the solution. The salt crystallises well from alcohol in needles melting and decomposing at 237°; on grinding with hydrochloric acid, the free acid is obtained. The acid crystallises from water in stellate clusters of prisms melting and decomposing at 169° (Found: C=53·83; H=4·94; N=5·38. $C_{12}H_{13}O_6N$ requires C=53·91; H=4·90; N=5·24 per cent.). The study of this acid is not yet completed.

Action of Concentrated Potassium Hydroxide on the Imide V.

The imide was treated with concentrated potassium hydroxide in exactly the same way as the dimethyl compound (see p. 1320). The mixture of acids obtained was dissolved in hot water, boiled with animal charcoal, filtered, and cooled, when a small amount of a crystalline solid separated. This melted at 229° and gave, on crystallisation from dilute alcohol, the flattened needles of the *trans-spiro*-acid melting at 238°. Its identity was confirmed by analysis (Found: C=60·85; H=7·25. Calc., C=60·57; H=7·12 per cent.), and by direct comparison with a genuine specimen. The anilide melting at 291° was also prepared from it.

The filtrate, on the addition of mineral acid, deposited the characteristic crystalline nodules of the lactonic acid (XVI).

In conclusion, the authors' thanks are due to Professor J. F. Thorpe, F.R.S., for his kind interest and advice during the progress of the investigation, and to the Salters' Institute of Industrial Chemistry for a grant to one of us (W. H. G.).

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CLII.—*The Ternary System Ammonium Chloride–Manganous Chloride–Water.*

By Frederick William Jeffrey Clendinnen and Albert Cherbury David Rivett.

The system ammonium chloride–manganous chloride–water has received a great amount of attention, probably because it is typical of a large number of cases in which mixed-crystal formation occurs between ammonium chloride and a hydrated chloride of a multivalent metal. There remain, however, some points worth further consideration.

Three double salts have been described, the respective molecular proportions of the components, in the order named in the title, being 1 : 1 : 2 (Hautz, *Annalen*, 1848, **66**, 285), 2 : 1 : 1 (Rammelsberg, *Pogg. Annalen*, 1855, **94**, 507; Pickering, T., 1879, **35**, 654) and 2 : 1 : 2 (Hauer, *J. pr. Chem.*, 1854, **63**, 436). Lehmann (*Zeitsch. Kryst. Min.*, 1883, **8**, 445) evidently recognised mixed-crystal formation. Saunders (*Amer. Chem. J.*, 1892, **14**, 127) endeavoured to prepare double salts and concluded that only the 2 : 1 : 2-compound was a definite substance. Various solids that he obtained he regarded as mechanical mixtures and, curiously enough, he did not consider the possibility of mixed-crystal formation. Johnsen (*Jahrb. Min.*, 1903, **2**, 93) studied the crystallography of the mixed crystals. The most systematic investigation so far carried out is by Foote and Saxton (*J. Amer. Chem. Soc.*, 1914, **36**, 1695). They worked only at 25° and claimed to have proved the existence of the double salt 2 : 1 : 2 and to have shown that this and ammonium chloride form two series of mixed crystals, there being a gap between the limiting compositions of each series.

It is unlikely that work at 25° will show the exact type of the system, since at this temperature $MnCl_2,2H_2O$, which is obviously the important hydrate of manganous chloride in this connexion, is not a stable phase in pure water or in dilute solutions of ammonium chloride. The consequence is that, at one end, the mixed-crystal system is obscured by the appearance of the stable tetrahydrate, $MnCl_2,4H_2O$, which does not enter into the formation of any compound or mixed crystal. As the invariant point, dihydrate–tetrahydrate–water, in the (condensed) binary system manganous chloride–water, is 57·85°, we have chosen to work at 60° and to apply the results obtained there to explain the 25° isotherm.

The experimental procedure is simple, including direct estimation of ammonium and chloride radicles by familiar methods and, in a few cases, of the manganese radicle as pyrophosphate.

Table I gives the figures obtained at 60° and these are shown plotted in the usual triangular method in Fig. 1.

TABLE I.

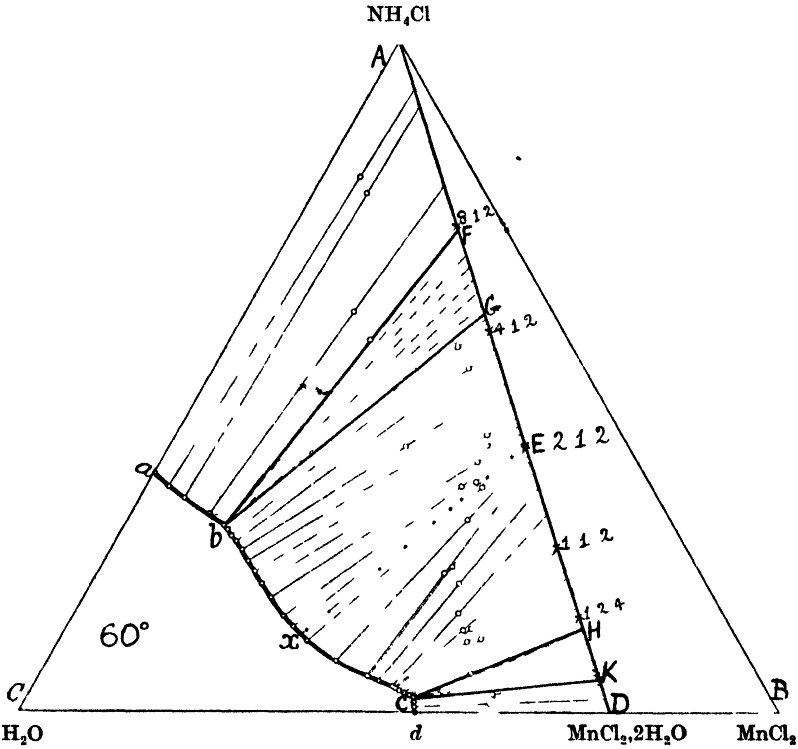
System at 60°

		Percentage composition.			
		Solution.		Residue.	
No.	Density.	NH_4Cl.	$MnCl_2$.	NH_4Cl.	$MnCl_2$.
1	1·105	33·52	2·91	79·77	5·04
2	1·129	31·93	5·84	77·37	7·03
3	1·183	29·50	10·16	59·70	14·10
4	1·192	27·81	12·95	55·53	18·32
5	1·200	27·07	13·79	47·90	25·68
6	1·214	25·94	15·16		
7	1·210	25·28	15·91	51·30	33·37
8	1·225	24·11	17·19	39·70	31·01
9	1·239	22·51	18·86	44·36	39·71
10	1·255	20·93	20·51	41·41	40·86
11	1·267	19·04	22·42	39·80	41·74
12	1·288	16·98	24·65	37·22	41·65
13	1·317	14·33	27·74	33·64	41·34
14	1·339	12·61	29·87	34·18	43·04
15	1·365	10·52	32·80	33·45	44·06
16	1·426	7·55	38·02	28·56	44·63
17	1·482	5·44	43·10	20·70	45·67
18	1·486	5·33	43·27	21·70	46·15
19	1·523	4·64	45·00	19·12	48·34
20	1·543	3·93	47·20	14·76	50·39
21	—	3·47	47·84	12·48	53·37
22	—	3·11	48·50	10·46	53·74
23	1·575	2·94	49·33	11·00	55·23
24	1·581	2·45	50·22	7·23	55·67
25	1·583	2·21	50·68	5·83	56·58
26	1·592	1·61	51·16	2·69	61·00
27	1·619	0·91	51·47	1·20	62·20

The residue method (Schreinemakers, *Zeitsch. physikal. Chem.*, 1893, **11**, 81) has been adopted in determining the compositions of solids in equilibrium with particular solutions. It has been taken as fully proved by previous workers that the solid phases lie on the line *AD* connecting the compositions of pure ammonium chloride and the dihydrate of manganous chloride.

It is clear from the figure that the system is one of a somewhat uncommon type of mixed crystals. Fixing attention first on the solid phases, one sees that there are three very well-defined series of mixed crystals, namely, *AF*, *GH*, and *KD*, with two gaps, *FG* and *HK*. The three curves *ab*, *bc*, and *cd* correspond with the series, respectively, and the intersections *b* and *c* with the gaps. The composition of the alleged compound 2 : 1 : 2 is at *E*, well within the second series *GH*. The line *AD* is, of course, simply a section across the temperature–concentration diagram of the binary system ammonium chloride–manganous chloride dihydrate at a temperature, 60°, which is below that at which any liquid phase may be formed.

FIG. 1.



The first interpretation suggesting itself is that there are here two binary systems linked together. The first is that extending from *A* to *E*, the components being ammonium chloride and 2 : 1 · 2; the second from *E* to *D*, the components being 2 : 1 : 2 and the dihydrate Each of these will correspond with either the fourth or fifth of Roozeboom's (*Zeitsch. physikal. Chem.*, 1889, **30**, 384) types of mixed crystal formation in binary systems. Foote and Saxton (*loc. cit.*), working only at 25°, recognised only the portion *AE*. We have supplemented their work and very com-

TABLE II.

em at 25°.

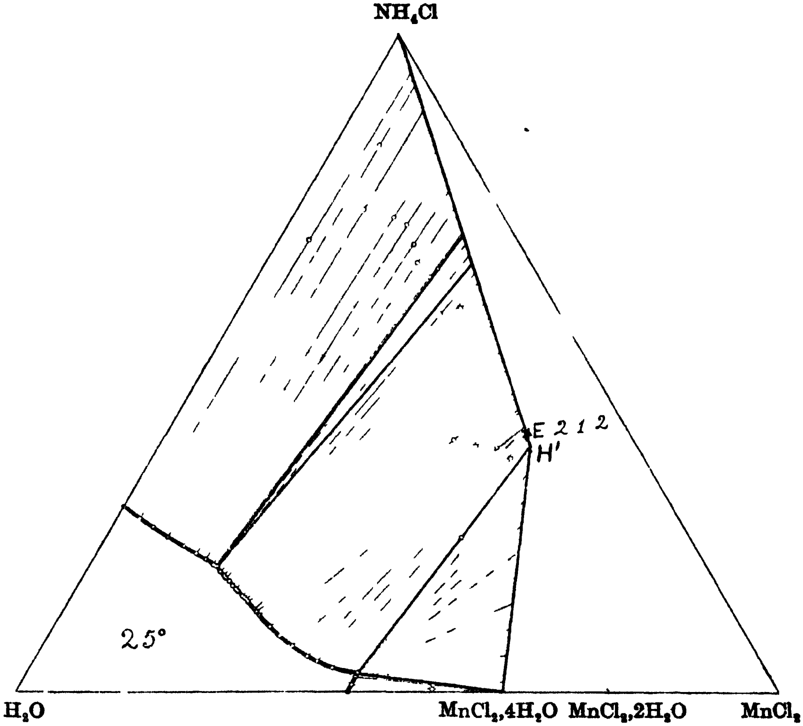
No.	Density.	Solution. NH$_4$Cl.	Solution. MnCl$_2$.	Residue. NH$_4$Cl.	Residue. MnCl$_2$.
1	1·077	28·33	—	—	—
2	1·101	26·47	3·01	68·97	3·92
3	1·119	25·11	5·37	83·37	5·76
4	1·140	23·71	7·89	73·57	8·74
5	1·164	22·35	10·70	72·44	13·19
6	1·181	21·12	13·00	71·43	15·36
7	1·200	20·30	14·62	68·16	17·89
8	1·209	19·48	16·04	65·54	19·70
9	1·215	19·09	16·78	64·60	22·91
10	1·216	19·07	16·57	63·32	22·36
11	1·222	18·37	17·54	57·87	26·54
12	1·227	17·77	18·16	56·67	27·79
13	1·230	17·40	18·71	58·44	28·66
14	1·237	16·90	19·39	55·72	30·35
15	1·245	16·35	20·14	54·44	32·40
16	—	15·76	20·92	46·95	30·97
17	1·255	15·41	21·42	—	—
18	1·263	14·84	22 17	41·02	33·64
19	1·265	14·54	22·58	36·40	33·11
20	1·268	14·26	23·02	45·54	38·19
21	1·270	14·13	22·98	44·70	37·91
22	1·273	13·82	23·43	38·59	37·88
23	1·286	12·69	24·83	42·80	41·64
24	1·292	12·22	25·33	31·33	36·87
25	1·297	11·77	25·98	37·66	41·23
26	1·317	10·00	28·07	37·30	44·16
27	1·338	8·56	30·16	32·00	41·55
28	1·362	7·05	32·65	35·96	44·68
29	1·396	5·53	35·42	28·97	42·93
30	1·413	4·86	37·02	30·65	44·90
31	1·448	3·85	39·53	35·73	46·66
32	1·494	2·95	43·11	23·55	46·39
33	1·494	2·95	43·22	2·18	54·34
34	1·492	2·26	43·28	1·08	53·97
35	1·490	1·31	43·31	0·63	54·18
36	1·485	—	43·45	—	—

pletely determined the 25° isotherm. The results are given in Table II and plotted in Fig. 2.

There can be no doubt whatever that even here mixed crystals of composition richer in MnCl$_2$,2H$_2$O than 2 : 1 : 2 do exist, extending, however, over only the comparatively small range *EH'*. The series ends at *H'* since thereafter the solid phase, MnCl$_2$,4H$_2$O, enters, a complication not showing itself at 60°. As a matter of fact, the figures of Foote and Saxton themselves clearly demonstrate this extension beyond 2 : 1 : 2, but these authors, who did not use the residue method but endeavoured always to obtain pure solid free from mother-liquor, failed to trust their own work sufficiently and suggested that the solids in equilibrium with the solutions at the latter part of the curve were really 2 : 1 : 2 from which they had only incompletely removed adhering liquor rich in manganese chloride.

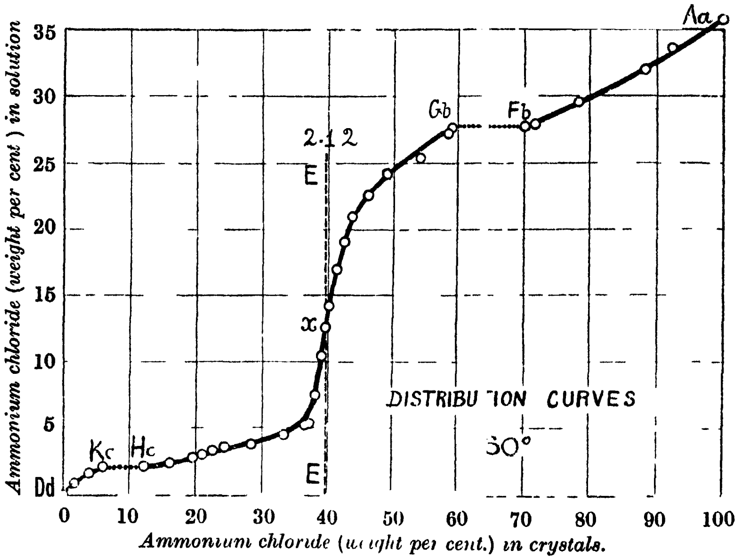
The 60° work definitely establishes the conclusion that the second series of mixed crystals does not stop at 2 : 1 : 2 (*E*) and the question arises as to whether even this last of the various alleged double salts may justly be called a compound. While it is true that there is a tendency for solutions over quite a considerable range about the middle of the curve to be in equilibrium with solids tending towards, or grouping themselves around, 2 : 1 : 2, yet, as can be seen from Fig. 1, there is no evidence at all that 2 : 1 : 2 exists as the stable solid phase with more than a single solution. This solution has a composition represented by a point at or near *x* in Fig. 1. If, however, it were a compound in the usual, although ill-defined, sense of the term, one would expect it to exist in equilibrium with a series of solutions, however small; not to change its composition with an infinitesimal change in the solution. One might indeed almost

FIG. 2.



as reasonably claim that 1 : 2 : 4, 1 : 1 : 2, 3 : 1 : 2, and 4 : 1 : 2 are definite compounds, since all fall along the line *GH*, and similarly other molecular proportions falling along *FA* or *KD*. The difference in the case of 2 : 1 : 2 is only that somewhere about this proportion does seem to be a more favoured grouping in the mixed crystals as shown by the spread of the tie-lines in its neighbourhood. This difference (which is only a difference of degree) appears perhaps more clearly when another method is adopted for plotting results, namely, that represented in Fig. 3 showing the distribution of ammonium chloride in co-existing phases.

FIG. 3.



Along rectangular axes are plotted percentages of ammonium chloride in solution and in the corresponding crystals, respectively. The horizontal dotted lines, *Kc*, *Hc*, and *Gb*, *Fb*, represent the gaps of Fig. 1. The existence of any particular solid with a series of solutions would show itself as a vertical line. There is no such line in the figure. The nearest approach to it is in the neighbourhood of the line *EE*, corresponding with the composition of 2 : 1 : 2; but it is quite clear that the experimental curve does not coincide with the vertical line at more than the single intersection point *x*.

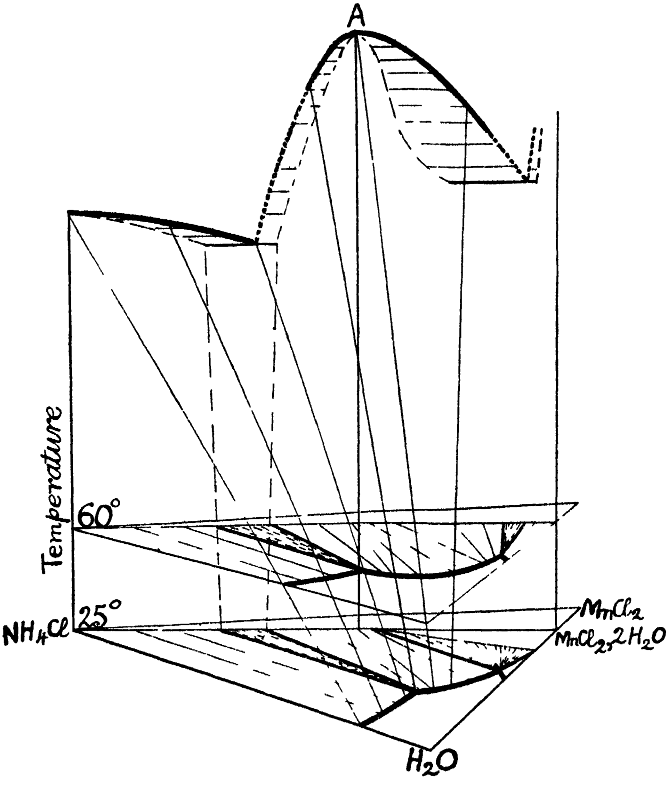
If, now, one restricts the term compound to a solid which may exist in equilibrium with a series of solutions, then clearly there is no justification for supposing a compound 2 : 1 : 2 to exist.

The question of the criteria of a definite solid compound is one of much interest from the point of view of the Phase Rule, and is perhaps best studied in a binary system. The line *AD*, as already stated, is an isothermal section of a binary system in which the two components are ammonium chloride and manganous chloride dihydrate, a system in which there are three series of mixed crystals and two gaps. It is easy to deduce from Roozeboom's (*loc. cit*) types with a single gap, or from isothermals of thermodynamic potential (ζ-function) and composition of solid and liquid, typical diagrams for temperature–composition relations in which two gaps exist between series of mixed crystals. At the changes of curvature in the liquidus curve there may be two transition or two eutectic points, or one of each. Owing to the instability of the components, the binary system ammonium chloride–dihydrate, cannot be investigated at temperatures at which liquid phases appear. It is thus not possible to ascertain directly the type of the system. One may, however, obtain some clue from a consideration of the ternary isotherms if one admits that the addition of water to the binary system of solids has an effect closely analogous to that of the addition of heat. In each case liquefaction is brought about as a main result. There are also other changes effected, such as ionic dissociation, which will differ more or less in the two cases, but consequent differences in other respects due to this may be qualitatively allowed for. Thus in the ternary concentration–temperature prism one may carry out an extrapolation from the 25° and 60° isotherms on to the temperature–composition plane of the binary system, ammonium chloride–manganous chloride dihydrate, in the manner represented quite diagrammatically in Fig. 4.

The portion at the dihydrate end cannot be traced below the entry of the tetrahydrate at 25°, nor can one be certain of other parts shown by dots where the extrapolation line falls on different curves at the respective temperatures. An extrapolation to the binary solidus curves offers difficulties, but making allowances as far as possible one may conclude that the binary system, if obtainable, would be one of two eutectics, with the corresponding solids somewhat as shown by the interrupted curves. The intermediate curve passes through a maximum. The maximum, as it happens, is as nearly as possible at 60·2 per cent. of manganous chloride dihydrate, which is the composition of 2 : 1 : 2. This might scarcely have been expected in such an extrapolation. The general type is quite a familiar one in metallography, although not so common in salt work.

Now the two-phase maximum point *A* is, from a phase-theory point of view, a one-component system, hence univariant. In the present case, the system is invariant because regarded as condensed. But this single degree of freedom might also be exercised in arbitrary selection (within limits) of a composition for the solid, or one for the liquid, phase, these being the other two variables. The pressure would then require to be adjusted to maintain the system. Putting this conversely, the composition at the maximum point might vary with the pressure, although no doubt such variation would be exceedingly slight. The case is indeed similar to that of a constant-boiling (maximum temperature) binary liquid mixture such as is obtainable from hydrogen chloride and water, although here the dependence on temperature is so marked that the term compound would never be applied even if the components were present in integral molecular proportions.

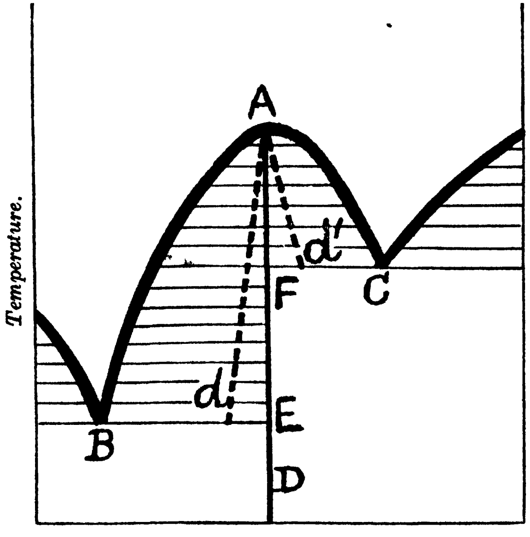
FIG. 4.



The question now arises as to whether a maximum ever does indicate a compound. The claim that it does so is made in those cases usually represented by a diagram such as Fig. 5.

The curve *BAC* gives solutions any one of which may be in equilibrium with solid of composition represented by the vertical line *AD*. Such a case, however, is theoretically impossible. The areas *ABE* and *AFC* are two-phase univariant (condensed) systems. Therefore if the composition of one phase, the solid, be fixed, both temperature and composition of the liquid are fixed. If *AE* and *AF* are vertical, this certainly cannot be the case. Hence each must have some inclination, however small, to the vertical, as shown by *Ad* and *Ad′*. *A* is thus always just a special member of a series of mixed crystals, and if a mixed crystal be something quite distinct from a compound, the latter term can never, strictly speaking be applied to the solid of composition of the maximum point. This is precisely the same point as that raised by Alkins (*Trans. Inst. Metals*, 1921, **25**, 209) in another connexion. He used it to conclude that any two metals cannot be perfectly immiscible in the solid state.

FIG. 5.



Composition.

The whole question becomes merely one of definition of terms and amounts simply to asking how near *Ad* and *Ad′* need approach to the vertical *AD* to justify the application of the term compound to the composition of *A*. Only an arbitrary answer is possible, but whatever it may be it is unlikely to allow so much deviation as to permit $2NH_4Cl,MnCl_2,2H_2O$ to be classed as a compound or double salt.

A few remarks may be made in conclusion regarding the formation of mixed crystals in these ternary solutions. It is obvious that only when the amount of solid formed is very small is the composition of the whole solid likely to be exactly that in equilibrium with the liquid. Otherwise the solid may be a succession of layers of different compositions, of which only the outer is in equilibrium with the liquid. We have always worked with complexes calculated to give only a small proportion of solid. Nevertheless, the limits of the gaps between series cannot be considered to have been exactly determined: nor are our tie-lines always identical with those of Foote and Saxton (*loc. cit.*), doubtless partly for the same reason. In addition, however, it has been proved that the composition of the mixed crystal varies for some hours with the time for which it has been in contact with the solution. It would seem as though a supersaturated solid solution, or mixed crystal, were at first formed, and that this then steadily rejected one of its constituents, the crystals undergoing fracture in the process. The following figures give an example at 60°.

	Percentage composition.			
Time of shaking.	Solution.		Solid (by extrapolation from solution and residue).	
	NH_4Cl	$MnCl_2$	NH_4Cl	$MnCl_2$
1 hour	29·8	9·7	77·3	17·5
24 and 96 hours	29·5	10·2	78·4	16·6

This is a fairly common phenomenon and will be mentioned again in the more striking case of the ternary system, ammonium chloride–ferric chloride–water, about which some considerations will be advanced in a subsequent paper.

Summary.

1. The 60° isotherm of the ternary system ammonium chloride–manganous chloride–water, shows three distinct curves in equilibrium respectively with three sets of mixed crystals, there being two gaps in the series of solids ranging from pure ammonium chloride to pure manganous chloride dihydrate.
2. The composition of the hitherto accepted compound $2NH_4Cl,MnCl_2,2H_2O$ occurs in the second or intermediate series of mixed crystals. At any selected temperature a solid of this composition can exist in equilibrium with one solution only. It is suggested that there is no justification for applying the term compound in such a case.
3. The 25° isotherm has been worked out and explained in accordance with deductions from that at 60°.

4. The probable type of the binary system ammonium chloride–manganous chloride dihydrate, is discussed and some considerations are advanced regarding the significance of maxima on concentration–composition curves.

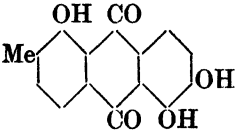
5. Some observations on the behaviour of mixed crystals are recorded.

UNIVERSITY OF MELBOURNE. [*Received, June 7th,* 1921.]

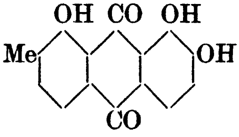
CLIII.—*Synthesis of* 1 : 6-*Dihydroxy-2-methylanthraquinone.*

By JOHN LIONEL SIMONSEN and MADYAR GOPAL RAU.

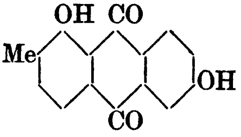
IN a recent communication (Simonsen, T., 1918, **113**, 766) it was suggested that morindone was most probably either hydroxymethylanthrarufin (I) or hydroxymethylchrysazin (II), the former formula being preferred.



(I.)



(II.)

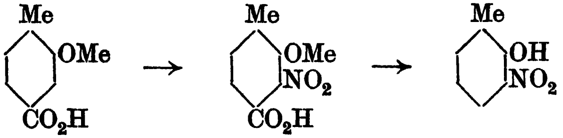


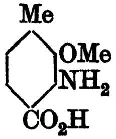
(III.)

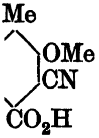
The only satisfactory method for differentiating between these two formulæ appeared to be by synthesis, and experiments in this direction were therefore undertaken, the results obtained forming the subject of this communication.

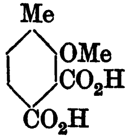
It was decided to attempt to prepare in the first place 1 : 6-*dihydroxy-2-methylanthraquinone* (III), since this substance, on the introduction of a third hydroxy-group by one of the methods which are usually successful in the anthraquinone series, would lead directly to the required hydroxymethylanthrarufin. The synthesis of 1 : 6-dihydroxy-2-methylanthraquinone was successful, but unfortunately all efforts to introduce the third hydroxy-group failed.

The first stage in the synthesis entailed the preparation of 3-*methoxy-4-methyl*-o-*phthalic acid* (IX), which, after a number of preliminary experiments, was ultimately found to be obtained most readily by the following series of reactions. When 2-methoxy-*p*-toluic acid (IV) was treated with nitric acid under the conditions described in the experimental part of this paper (p. 1342), it was converted quantitatively into 3-*nitro*-2-*methoxy*-p-*toluic acid* (V). The constitution of this nitro-acid was determined by the elimination of the carboxyl group and subsequent hydrolysis of the nitromethoxycresol with formation of 3-nitro-*o*-cresol (VI).


(IV.) (V.) (VI.)

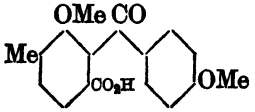

(VII.)

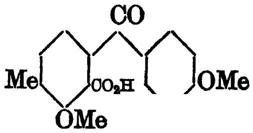

(VIII.)

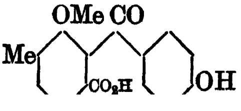

(IX.)

The formation of this nitro-acid was somewhat unexpected, and is another example of the powerful orientating influence exercised by methoxy-groups, to which attention has already been directed by the authors (T., 1917, **111**, 220; 1918, **113**, 22). 3-Nitro-2-methoxy-*p*-toluic acid on reduction was converted into the *amino*-acid (VII), and this, when diazotised and treated with cuprous cyanide, gave 2-*methoxy*-3-*cyano*-p-*toluic acid* (VIII). It was anticipated that considerable difficulty would be experienced in hydrolysing the cyano-acid, but contrary to expectation the acid on boiling with water (see p. 1344) yielded the required phthalic acid (IX). So far as the authors are aware, no case is known in which a cyano-acid with two substituents in the ortho-positions undergoes hydrolysis with such remarkable ease (compare Sudborough, T., 1895, **67**, 601; Sudborough, James, and Lloyd, *ibid.*, 1897, **71**, 229; Cain, *Ber.*, 1895, **38**, 969).

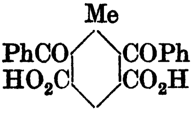
3-*Methoxy*-4-*methylphthalic anhydride* was condensed with anisole by means of aluminium chloride in the usual manner. It is obvious that the condensation can proceed with the formation of either 2 : 4′-dimethoxy-3-methylbenzophenone-6-carboxylic acid (X) or 3 : 4′-dimethoxy-4-methylbenzophenone-2-carboxylic acid (XI).


(X.)

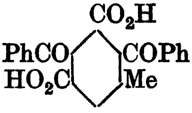

(XI.)


(XII.)

The acid resulting from the aluminium chloride reaction was found to be quite homogeneous, although partial hydrolysis had taken place with formation of a *hydroxymethoxy-acid* which we consider to be most probably represented by formula (XII), the corresponding *methyl ether* having formula (X). A large number of experiments were made with the object of obtaining direct evidence in support of this view, but all attempts to eliminate the carboxyl group with formation of the benzophenone were unsuccessful.* The main evidence in support of formula (X) as opposed to formula (XI) was the fact that the acid was readily methylated by the Victor Meyer method with formation of the corresponding methyl ether. Further, the acid was found to be extremely stable and could be heated far above its melting point without loss of carbon dioxide, a property not usually found in acids having a carboxyl group in the ortho-position to hydroxy- or methoxy-groups. It is recognised that this cannot be regarded as an absolute proof, since it has been shown by Graebe (*Ber.*, 1900, **33**, 3026)



(XIII.)



(XIV.)

and by Mills and Easterfield (T., 1902, **81**, 1313) that the two isomeric dibenzoyluvitic acids (XIII) and (XIV) are both readily methylated by methyl alcohol and hydrochloric acid.†

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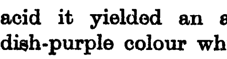
* 2 : 4-*Dimethoxy*-3-*methylbenzophenone* was obtained as an oil by the condensation of 2-methoxy-*m*-toluoyl chloride and anisole; 3-4′-*dimethoxy*-4-*methylbenzophenone*, prepared from 2-*methoxy*-p-*toluoyl chloride* and anisole, crystallised from methyl alcohol in prisms melting at 77—78° (Found: C=74·6; H=5·9. $C_{16}H_{16}O_3$ requires C=75·0; H=6·2 per cent.).

† Preliminary experiments on the condensation of hemipinic anhydride and *o*-cresol by the method recently described by Ullmann and Schmidt (*Ber.*, 1919, **52**, [*B*], 2098) have shown that the main product of the reaction was an *acid* melting at 251—252° (Found: C=64·3; H=4·8. $C_{17}H_{16}O_6$ requires C=64·5; H=5·1 per cent.). This acid is in all probability 2′-*hydroxy*-2 : 3-*dimethoxy*-3′-*methylbenzophenone*-6-*carboxylic acid* (XV), since when



(XV.)

warmed with sulphuric acid it yielded an anthraquinone dissolving in sulphuric acid with a reddish-purple colour which on the addition of boric acid became deep purple, a colour reaction characteristic of hydroxychrysazin derivatives, since hydroxyanthrarufin derivatives yield a blue colour on addition of boric acid to a sulphuric acid solution. The formation of this acid tends to support the formula (X) ascribed to the acid obtained by the condensation of anisole and 3-methoxy-4-methyl-*o*-phthalic acid, since in both cases it is the 2-carboxyl group which reacts.

The benzoylbenzoic acid was readily converted by treatment with sulphuric acid into 1 : 6-*dimethoxy*-2-*methylanthraquinone* (III). All attempts to introduce a third hydroxy-group into the molecule were, however, unsuccessful and in view of the difficulty of preparing the anthraquinone in quantity further experiments in this direction were abandoned.

EXPERIMENTAL.

3-*Nitro*-2-*methoxy*-p-*toluic Acid* (V).

Finely powdered 2-methoxy-*p*-toluic acid * (6 grams) was slowly added to a mixture of nitric acid (*d* 1·5) (12 grams) and acetic anhydride (24 grams), the mixture being well cooled in ice-water. The acid readily dissolved, and after remaining for about fifteen minutes, during which time the temperature was allowed to rise to between 20° and 30°, the reaction mixture was poured on to ice, when an oil separated which rapidly solidified. The acid was collected and a further quantity separated from the filtrate on saturation with ammonium sulphate (yield 7 to 8 grams).

The nitro-acid, which was found to be homogeneous, was purified by crystallisation from a large quantity of hot water, when it separated in long, prismatic needles melting at 165—166° (Found : N=6·8. $C_9H_9O_5N$ requires N=6·6 per cent.).

3-*Nitro*-2-*methoxy*-p-*toluic acid* was somewhat readily soluble in hot water, but much more sparingly soluble in cold; it was found to be readily soluble in all the ordinary organic solvents.

The *amide*, which was prepared from the *acid chloride* in the usual manner, crystallised from hot water in long, colourless needles melting at 142° (Found: N=13·7. $C_9H_{10}O_4N_2$ requires N=13·3 per cent).

3-*Nitro*-2-*methoxy*-p-*toluidine*.—For the preparation of this substance the amide (1·5 grams) was added gradually to a well-cooled solution of bromine (0·8 gram) in potassium hydroxide solution (35 c.c.) (1·7 grams of KOH). The amide rapidly passed into solution and on warming on the water-bath an orange-coloured oil separated. This was extracted with ether and the ether dried and evaporated, when the *base* was obtained as a viscid, orange-yellow oil which did not solidify. The *acetyl* derivative, prepared in the usual manner, crystallised from hot water in colourless needles which melted at 92—93° (Found: N=12·6. $C_{10}H_{12}O_4N_2$ requires N=12·5 per cent.).

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* Methyl 2-methoxy-*p*-toluate (compare Perkin and Weizmann, T., 1906, **89**, 1658) was obtained in prismatic needles melting at 51—52° (Found: C=67·0; H=6·5. Calc., C=66·6; H=6·6 per cent.).

Diazotisation of 3-*Nitro*-2-*methoxy*-p-*toluidine.*

3-*Nitro*-o-*cresol.*—The base (1 gram) was dissolved in a mixture of alcohol (10 c.c.) and sulphuric acid (0·8 gram) and the well-cooled solution treated with amyl nitrite (1·5 grams). When the reaction was complete, the mixture was heated on the water-bath until all evolution of nitrogen had ceased, water added, and the nitrotolyl methyl ether extracted with ether.

The methyl ether, which was an oil, was identified by conversion into the cresol by hydrolysis with hydrochloric acid at 140°. The 3-nitro-*o*-cresol thus obtained was purified by distillation in steam, when it separated in yellow needles melting at 69·5°, and this melting point was not altered on admixture with a specimen of the nitrocresol from another source.

1-*Methoxy*-2-*methylphenanthraphenazine.*—A further proof of the constitution of the above-mentioned nitroamine was furnished by its reduction to the corresponding *diamine* by tin and hydrochloric acid in the usual manner. This was converted into the phenanthraphenazine by the method described by Jones and Robinson (T., 1917, **111**, 924). This substance crystallised from acetic acid in felted, yellow needles melting at 187°. It dissolved in concentrated sulphuric acid, yielding a magenta-coloured solution; a neutral solution exhibited no fluorescence (Found: N=9·0. $C_{22}H_{16}ON_2$ requires N=8·6 per cent.).

3-*Amino*-2-*methoxy*-p-*toluic Acid* (VII).

If the following conditions are closely adhered to, an excellent yield of the *amino*-acid may be obtained. The nitro-acid (10 grams) was dissolved in concentrated ammonia (25 c.c.) and added gradually to a solution of ferrous sulphate (80 grams) in water (140 c.c.), the mixture being kept on a vigorously boiling water-bath until all reaction had ceased. The filtrate (the residue should be washed with the minimum quantity of hot water) was evaporated on the water-bath until the *ammonium* salt began to separate from the hot solution, filtered from a trace of tar, and made just acid with dilute hydrochloric acid, when the *amino*-acid separated (yield 7·5 grams).

3-*Amino*-2-*methoxy*-p-*toluic acid* separated from hot water, in which it was somewhat readily soluble, in long, prismatic needles melting at 162°. For analysis it was dried at 115° (Found: C=59·6; H=6·0; N=7·6. $C_9H_{11}O_3N$ requires C=59·7; H=6·1; N=7·7 per cent.). The acid was readily soluble in alcohol, ethyl acetate, or acetone, moderately soluble in hot water, but only sparingly so in cold water, benzene, or light petroleum. Both the *hydrochloride* and *sulphate* were somewhat sparingly soluble in cold water, the former crystallising in rhombic plates, the latter in minute needles.

The *platinichloride* was obtained in straw-coloured needles, which decomposed at 220° (Found: Pt=25·2. $(C_9H_{11}O_3N)_2,H_2PtCl_6$ requires Pt=25·3 per cent.).

The *acetyl* derivative crystallised from hot water in long needles melting at 191°. It was found to be readily soluble in most of the ordinary organic solvents.

2-*Methoxy*-3-*cyano*-p-*toluic Acid* (VIII).

The amino-acid (1 gram) was dissolved in hydrochloric acid (*d* 1·18) (1·5 c.c.) and water (5 c.c.) and the ice-cold solution treated with an aqueous solution of sodium nitrite ($NaNO_2$ 0·4 gram). When diazotisation was complete, the solution was filtered and added to a hot solution of potassium cyanide (1·6 grams) and copper sulphate (1·4 grams) in water (20 c.c.). All evolution of nitrogen having ceased, the mixture was cooled, rendered acid to congo-paper with dilute hydrochloric acid, and allowed to remain in the cold for several hours. The mixture of the *cyano*-acid and cuprous cyanide which had separated was collected, dissolved in dilute ammonia, the solution filtered, and the filtrate acidified, when the cyano-acid was deposited as an almost colourless, crystalline mass (yield 0·9 gram). For analysis, it was purified by crystallisation from dilute methyl alcohol, when it was obtained in slender needles melting at 186° (Found: C=62·7; H=4·8; N=7·5. $C_{10}H_9O_3N$ requires C=62·8; H=4·7; N=7·3 per cent.).

2-*Methoxy*-3-*cyano*-p-*toluic acid* was found to be readily soluble in the majority of organic solvents; it was sparingly soluble in cold water, more readily soluble in hot. When the aqueous solution of the cyano-acid was boiled, hydrolysis gradually took place with formation of the phthalic acid.

The *silver* salt crystallised from hot water in short, prismatic needles (Found: Ag=36·0. $C_{10}H_8O_3NAg$ requires Ag=36·2 per cent.).

3-*Methoxy*-4-*methyl*-o-*phthalic Acid and its Anhydride* (IX).

The *anhydride* was readily prepared by heating the cyano-acid (3 grams) with sulphuric acid (75 per cent.) (4·5 c.c.) on the water-bath for three hours. On pouring on to ice, the anhydride separated as a white, crystalline powder, which was purified by crystallisation from toluene (Found: C=62·4; H=4·4. $C_{10}H_8O_4$ requires C=62·5; H=4·2 per cent.).

3-Methoxy-4-methyl-o-phthalic anhydride separated from toluene in long needles melting at 135°. It was found to be readily soluble in acetic acid or chloroform; in cold water, it was sparingly soluble, more readily soluble in hot, being converted into the acid on boiling the solution.

When the mother-liquor from which the anhydride had been separated was saturated with hydrogen chloride, the *phthalic acid* was precipitated. It was purified by crystallisation from a small quantity of hot water (Found: C=56·9; H=4·7. $C_{10}H_{10}O_5$ requires C=57·1; H=4·8 per cent.).

3-Methoxy-4-methyl-o-phthalic acid crystallised in short prisms which decomposed at about 175—176° with formation of the anhydride, the decomposition point being found to vary somewhat with the rate of heating. It was readily soluble in most organic solvents with the exception of chloroform and was somewhat sparingly soluble in cold water.

The *barium* salt crystallised in fine needles which were somewhat sparingly soluble in hot water, whilst the *silver* salt was obtained in minute prisms (Found: Ag=50·9. $C_{10}H_8O_5Ag_2$ requires Ag=51·0 per cent.).

The *imide* was readily obtained when the anhydride was treated with ammonia, the temperature being gradually raised during the course of three hours from 130° to 250°. It was purified by sublimation and finally by crystallisation from dilute methyl alcohol, from which it separated in small needles melting at 228°. It was very sparingly soluble in water, ether, benzene, or light petroleum, and readily soluble in chloroform or acetic acid (Found: C=62·9; H=4·9. $C_{10}H_9O_3N$ requires C=62·8; H=4·7 per cent.).

Condensation of 3-Methoxy-4-methyl-o-phthalic Anhydride and Anisole. 4′-Hydroxy-2-methoxy-3-methylbenzophenone-6-carboxylic Acid (XII).

In one experiment the anhydride (1 gram) was dissolved in anisole (10 c.c.) and freshly-prepared aluminium chloride (2 grams) was gradually added to the mixture. A vigorous reaction took place, and after heating on the water-bath for two to three hours, when all evolution of hydrogen chloride had ceased, the deep red mixture was cooled, treated with ice-water, and the excess of anisole removed in steam. On keeping, the residual liquor deposited a pink, crystalline powder, which was collected and drained on porous porcelain (yield 1·5 grams). The crude acid was dissolved in dilute sodium hydroxide solution, filtered to remove a trace of tar, and the solution acidified with dilute hydrochloric acid, when the *benzophenonecarboxylic acid* separated as a pasty mass which slowly crystallised. It was purified by crystallisation from dilute methyl alcohol, from which it separated in balls of radiating needles * (Found: C=67·1; H=4·7; OMe=10·8. $C_{15}H_{11}O_4 \cdot OMe$ requires C=67·1; H=4·9; OMe=10·9 per cent.).

4′-*Hydroxy*-2-*methoxy*-3-*methylbenzophenone*-6-*carboxylic acid* melted at 218°. It was very sparingly soluble in water, toluene, or chloroform and more readily soluble in methyl alcohol, acetone, or acetic acid. Its alcoholic solution gave no colour with ferric chloride solution.

The *silver* salt was obtained as a caseous, white precipitate (Found: Ag=27·4. $C_{16}H_{13}O_5Ag$ requires Ag=27·5 per cent.).

Methyl 2 : 4′-*Dimethoxy*-3-*methylbenzophenone*-6-*carboxylate*.—The following method was found to be the most convenient for the preparation of this substance. The crude hydroxy-acid (5 grams) was mixed with methyl alcohol (15 c.c.) and potassium hydroxide solution (50 per cent.) (4 c.c.) and after the addition of methyl iodide (5·8 grams) the mixture was heated in a soda-water bottle for six hours on the water-bath. On cooling, crystals of the methyl ether were observed to have separated. These were collected, washed with a little dilute alkali, and dried (yield 5 grams). A further quantity of a less pure product can be obtained by the addition of water to the mother-liquor.

The *methyl* ether crystallised from methyl alcohol in colourless, prismatic needles melting at 162°. It was insoluble in water and only sparingly soluble in cold methyl alcohol. In the ordinary organic solvents it was readily soluble (Found: C=68·5; H=5·5; OMe=29·8. $C_{16}H_{12}O_3[OMe]_2$ requires C=68·4; H=5·7; OMe=29·6 per cent.).

2 : 4′-*Dimethoxy*-3-*methylbenzophenone*-6-*carboxylic Acid* (X).

This acid was readily obtained by hydrolysing the above-mentioned methyl ether with alcoholic potassium hydroxide solution. After removing the alcohol on the water-bath, the aqueous solution was acidified, when the acid separated as a colourless, crystalline powder.

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* The hydroxybenzophenonecarboxylic acid was frequently contaminated with the corresponding methyl ether, which rendered its purification somewhat difficult; in the preparation of large quantities it was therefore not purified, but converted into *methyl* 2 : 4′-*dimethoxy*-3-*methylbenzophenone*-6-*carboxylate*. From the mother-liquor from which the benzophenonecarboxylic acid had been separated a small quantity of a neutral substance, crystallising in needles and melting at 100—115°, was extracted by ether. This has not been further investigated.

It was purified by crystallisation from dilute acetic acid, when it separated in small needles melting at 205—206° (Found : C=68·2; H=5·3; OMe=20·6. $C_{15}H_{10}O_3(OMe)_2$ requires C=68·0; H=5·3; OMe=20·7 per cent.).

2 : 4′-*Dimethoxy-3-methylbenzophenone-6-carboxylic acid* was found to be readily soluble in the ordinary organic solvents, but very sparingly soluble in hot water.

The *silver* salt, prepared in the usual manner, was obtained as a caseous, white precipitate (Found : Ag=26·8. $C_{17}H_{15}O_5Ag$ requires Ag=26·5 per cent.). The acid was found to be readily esterified by V. Meyer's method. In one experiment the acid (0·5 gram) was dissolved in methyl alcohol (10 c.c.) and the ice-cold solution saturated with hydrogen chloride. On standing, crystals of the methyl ester gradually separated (0·3 gram) and melted sharply at 162°. As has been mentioned in the introduction (p. 1341), the ready esterification of this acid is strong evidence in favour of the view that it is 2 : 4′-dimethoxy-3-methylbenzophenone-6-carboxylic acid.

1 : 6-*Dimethoxy-2-methylanthraquinone* (III).

For the preparation of this substance, the following method was found to be the most convenient. The foregoing benzophenonecarboxylic acid (1 gram) was dissolved in sulphuric acid (4 c.c.) and after the addition of phosphoric oxide (0·5 gram), the mixture was heated for half an hour at 140—150°. The deep red solution was poured into water and the dirty yellow precipitate which separated was collected, heated with potassium hydroxide solution to remove a considerable quantity of hydroxyanthraquinone which had been formed, and the crude dimethoxyanthraquinone purified by repeated crystallisation from benzene (Found : C=72·2; H=4·8. $C_{17}H_{14}O_4$ requires C=72·4; H=4·9 per cent.).

1 : 6-*Dimethoxy-2-methylanthraquinone* crystallised from benzene in yellow needles melting at 182°. It dissolved in sulphuric acid with a deep red colour.

The alkaline washings from which the dimethoxyanthraquinone had been separated were acidified and the hydroxyanthraquinone was purified by conversion into the *acetyl* derivative, which crystallised from acetic acid or alcohol in sulphur-yellow needles melting at 212° (Found : C=67·2; H=4·1. $C_{19}H_{14}O_6$ requires C=67·4; H=4·1 per cent.).

1 : 6-*Dihydroxy-2-methylanthraquinone,* which was obtained by the hydrolysis of the pure acetyl derivative, crystallised from acetic acid, in which it was somewhat sparingly soluble, in brown, bayonet-

shaped needles melting at 281°. It dissolved in alkali and in sulphuric acid with a red colour (Found: C=70·6; H=3·9. $C_{15}H_{10}O_4$ requires C=70·9; H=3·9 per cent.).

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CLIV.—*Cupritartrates.*

By John Packer and Ian William Wark.

Compounds containing complex negative cupritartrate radicles were first isolated by Werther (*Jahresber.*, 1844, 432). He prepared two compounds, a neutral one, $Na_2Cu_3C_8H_8O_{14},7H_2O$, and another, $Na_2CuC_4H_2O_6,5H_2O$, presumably identical with the mono-tartrate subsequently described by Bullnheimer and Seitz.

Masson and Steele (T., 1899, **75**, 725) described and analysed the potassium, silver, and lead salts of an acid, $H_3Cu_4C_{12}H_9O_{19}$. Although the acid was too unstable to be prepared, the salts were all stable with the exception of the silver salt, which darkened on exposure to light, and it was shown by electrolytic experiments that the copper was present in the negative radicle. The neutral potassium salt was obtained from a saturated solution of copper tartrate in dilute potassium hydroxide solution, and it was found that five molecules of potassium hydroxide are able to dissolve four of copper tartrate. The other salts were prepared by double decomposition.

Bullnheimer and Seitz (*Ber.*, 1899, **32**, 2347; 1900, **33**, 817) state that these neutral compounds are unstable and that the sodium salt is not the salt of Fehling's solution. Alkaline potassium, sodium, and lithium cupritartrates were prepared in the presence of excess alkali, and analysed. Two series of compounds were obtained.

1. Monotartrates of the type $M'_2CuC_4H_2O_6+xH_2O$.
2. Ditartrates of the type $M'_2CuC_4H_2O_6,M'_4C_4H_2O_6+xH_2O$.

Pickering (T., 1911, **99**, 169, and subsequent papers) prepared the sodium and potassium representatives of several new types of cupritartrates, most of which are unstable. In no case was a complete analysis given, the percentage of alkali metal and copper only being determined. Nevertheless, an attempt was made to explain the structure of these compounds on the basis of the assumed quadrivalency of copper. The compounds were obtained from solutions containing various proportions of sodium hydroxide, sodium carbonate, sodium tartrate or racemate, and copper hydroxide, and often it was difficult or impossible to purify them.

Pickering obtained different values (5 : 4 and 4 : 3) for the number of molecules of alkali needed to dissolve one molecule of copper tartrate with the production of an exactly neutral solution, according as the alkali was or was not specially prepared free from carbonate. From the neutral solutions thus obtained, a compound in which the atomic ratio Na : Cu was 2 : 3 was separated. This corresponds with Werther's compound, but not with that of Masson and Steele, in which the ratio was 3 : 4. Pickering later prepared, from a solution of copper racemate in sodium hydroxide, a compound yielding the latter ratio, but states that the 2 : 3-compound is much easier to obtain.

Schiff (*Annalen*, 1862, **123**, 46) was the first to describe a compound obtained from a solution of copper tartrate in ammonia. He obtained it in the form of a blue glass, to which he assigned the formula $CuC_4H_4O_6,4NH_3$. The dihydrate was also prepared by Bullnheimer and Seitz in a crystalline form. They also describe another compound containing less ammonia. In both papers it is assumed that the copper is present in the positive ion, and that these compounds are typical tetra-amminecupric salts with the positive ion $Cu(NH_3)_4^{\cdot\cdot}$.

In view of these somewhat conflicting reports it seemed advisable to undertake an investigation of cupritartrates, more especially in connexion with the neutral salts.

The following neutral cupritartrates have been prepared and analysed.

Sodium α-cupritartrate, $Na_3Cu_4C_{12}H_9O_{19},11H_2O$.

Barium α-cupritartrate, $Ba_3(Cu_4C_{12}H_9O_{19})_2,27H_2O$.

Ammonium α-cupritartrate, $(NH_4)_3Cu_4C_{12}H_9O_{19},9H_2O$.

These correspond with Masson and Steele's compounds.

Ammonium β-cupritartrate, $(NH_4)_2Cu_3C_8H_6O_{13},6H_2O$.

This corresponds with Werther's sodium salt, and with the neutral sodium and potassium compounds of Pickering.

The α-cupritartrates are the most stable of all the cupritartrates. They show no signs of decomposition on keeping in the solid state or in solution. The solutions are stable to carbon dioxide, and are not affected by boiling, nor will they, like alkaline cupritartrates, oxidise glucose. They cannot, therefore, be regarded as the active principles of Fehling's solution.

Synthetic experiments, in which the volume of *N*/3-sodium hydroxide solution just necessary to dissolve a known weight of pure copper tartrate was found, were carried out as described by Masson and Steele, and their results were fully confirmed (namely,

$5NaOH : 4CuC_4H_4O_6$). Pickering's ratio ($4NaOH : 3CuC_4H_4O_6$) would be required for the production of those compounds which contain alkali metal and copper in the atomic ratio 2 : 3, for example, ammonium β-cupritartrate.

Schiff's alkaline ammonium salt has been obtained from solution as a hydrate, $Cu(NH_3)_4C_4H_4O_6,H_2O$, and also by passing ammonia gas over ammonium α-cupritartrate. It has been shown by electrolytic experiments that copper is present in the negative, and not in the positive, ion in all these ammonium salts.

From the solution of sodium α-cupritartrate in sodium hydroxide, a few, definite, crystalline, alkaline compounds have been obtained, but most of them slowly undergo spontaneous decomposition. A very large number of cupritartrates undoubtedly exist, and, as a general rule, one may say that the more alkali they contain, the more unstable they are, and the more readily hydrolysed in solution. This is quite parallel to the case of the ammonium compounds, the more alkaline of which readily dissociate, giving off ammonia. All are oxidising agents and Fehling's solution, with its excess of alkali, must contain one or more of them.

Copper tartrate in the presence of alkali metal tartrates gives deep blue solutions. An attempt to obtain these soluble complexes in the solid form failed because the compounds are stable only in the presence of a large excess of the latter salts.

EXPERIMENTAL.

A. Neutral Cupritartrates.

(1) *Sodium α-Cupritartrate.*—To a saturated solution of copper tartrate in *N*/3-sodium hydroxide solution ($5NaOH : 4CuC_4H_4O_6$) absolute alcohol was added slowly with constant stirring (2 vols. of alcohol to 1 vol. of solution). A fine blue, crystalline precipitate of sodium cupritartrate was thus obtained.

$$5NaOH + 4CuC_4H_4O_6 = Na_2C_4H_4O_6 + Na_3Cu_4C_{12}H_9O_{19} + 4H_2O.$$

The precipitate was freed from sodium tartrate by washing with a 65 per cent. solution of alcohol, in which the blue crystals are insoluble. These crystals were dissolved, reprecipitated, and washed again, finally with absolute alcohol, and then dried on a porous tile in the air. Larger crystals can be obtained by allowing slow diffusion of absolute alcohol into the solution of cupritartrate (Found: Na=7·10, 6·98; Cu=25·63, 25·73; C=14·71, 14·73; H=3·30, 3·39; loss in a vacuum over concentrated sulphuric acid=20·34. $Na_3Cu_4C_{12}H_9O_{19},11H_2O$ requires Na=7·05; Cu=25·99; C=14·73; H=3·19; H_2O=20·25 per cent.).

In the analysis of these compounds the carbon was estimated by fusion with a lead chromate–potassium dichromate mixture, and the hydrogen in a separate combustion. Copper was estimated electrolytically, and sodium as sulphate, after ignition to destroy the organic matter.

(2) *Barium α-cupritartrate* was prepared as a pale blue, heavy, granular precipitate by double decomposition between solutions of barium chloride and sodium cupritartrate in equivalent proportions, the cupritartrate solution being slowly added to the other. The compound was washed free from chloride with water, in which it is only very slightly soluble, and dried in the air. It is soluble in excess of sodium cupritartrate solution (Found: Ba=16·70; Cu=22·20; C=12·54; H=3·45. $Ba_3Cu_8C_{24}H_{18}O_{38},27H_2O$ requires Ba=17·75 Cu=21·92; C=12·41; H=3·13 per cent.).

(3) *Neutral Ammonium α-Cupritartrate.*—It is possible to obtain this compound in several different forms. Complete saturation of a strong ammonia solution with copper tartrate until the reaction is quite neutral requires several weeks. Addition of absolute alcohol to the dark blue solution thus produced precipitates a blue, gummy substance. The adherent liquid is partly removed by pressing, when the mass acquires a beautiful lustre and becomes exceedingly sticky. By successive applications of absolute alcohol all the water is removed and, on rubbing, the mass quickly solidifies.

If dilute alcohol be used for the precipitation, a fine amorphous form is obtained, which cannot be retained by a filter paper. Rubbing under absolute alcohol causes this precipitate to change into larger grains, which are quite easily filtered.

If exposed to the air after washing with 60 per cent. alcohol (in which it is insoluble), the whole dissolves in the water left on evaporation of the alcohol and finally dries to a hard, amorphous, glassy mass.

A crystalline form of the salt was prepared for analysis as follows. Absolute alcohol was added to a saturated solution of copper tartrate in ammonia until incipient crystallisation occurred. On standing, a good crop of blue crystals was deposited. These were washed with 60 per cent. alcohol, dissolved in water, and reprecipitated in order to ensure purity. The crystals were finally washed with absolute alcohol, which was removed by drying on a porous tile in a desiccator containing 80 per cent. alcohol. They were stable in the air on a dry day, but hygroscopic in moist weather. The compound gives the same precipitates with salts of the heavy metals, as does sodium α-cupritartrate (Found: N=4·55; Cu=27·50; C=15·52; H=4·55. $(NH_4)_3Cu_4C_{12}H_9O_{19},9H_2O$ requires N=4·53; Cu=27·41; C=15·52; H=4·24 per cent.).

B. Ammonium Cupritartrates.

(1) *Neutral ammonium α-cupritartrate* has already been described under A.

(2) *Neutral Ammonium β-Cupritartrate.*—This was obtained in an attempt to prepare a fresh sample of the α-compound. The ammonia solution used was less concentrated than formerly, the copper tartrate was not in contact with the ammonia for so long a period, and the crystals were not dried so rapidly. No other explanation can be offered for the production of a different compound, and the relationship between these compounds has not been more fully investigated at present [Found: $N=4\cdot36$; $Cu=29\cdot19$; $C=15\cdot17$; $H=4\cdot45$. $(NH_4)_2Cu_3C_8H_6O_{13},6H_2O$ requires $N=4\cdot34$; $Cu=29\cdot57$; $C=14\cdot89$; $H=4\cdot06$ per cent.].

The small discrepancies are accounted for if we assume the presence of a small amount of the α-compound as impurity.

The equation for the synthesis may be written

$$4NH_4{\cdot}OH+3CuC_4H_4O_6= (NH_4)_2C_4H_4O_6+(NH_4)_2Cu_3C_8H_6O_{13}+3H_2O.$$

(3) *Alkaline Ammonium Cupritartrate* (Schiff's Salt).—When ammonia in excess is added to the neutral solution of copper tartrate in ammonia, a deeper violet-blue solution is obtained; this may be taken to indicate the production of a new compound. If a small amount of absolute alcohol be added to this solution, beautiful, violet-blue crystals are deposited. If the solution is sufficiently concentrated, crystals can be obtained without the addition of alcohol. Sometimes an oily layer containing the salt separates instead of the crystals, but stirring with absolute alcohol and concentrated ammonia causes crystallisation. On standing overnight, a solution brought to incipient crystallisation by addition of alcohol deposits a large crop of well-formed crystals. For analysis these were dissolved and reprecipitated (by "seeding"), washed with a mixture of alcohol and ammonia and finally with alcohol and ether, and dried over sodium hydroxide in a desiccator (Found: $N=18\cdot30$; $Cu=21\cdot30$; $C=16\cdot14$; $H=6\cdot26$. $Cu(NH_3)_4C_4H_4O_6,H_2O$ requires $N=18\cdot82$; $Cu=21\cdot36$; $C=16\cdot13$; $H=6\cdot09$ per cent.).

The compound very readily dissociates when in the crystalline form, giving off ammonia. Schiff describes his compound as being stable in air; he, however, prepared it in the form of a glass, from the interior of which ammonia would be unable to escape.

The compound may also be prepared by the action of dry ammonia gas on the neutral ammonium α-compound according to the equation, as shown by quantitative experiments.

$$(NH_4)_3Cu_4C_{12}H_9O_{19},9H_2O+13NH_3= 3Cu(NH_3)_4C_4H_4O_6,H_2O+Cu(NH_3)_4(OH)_2+7H_2O.$$

(4) *Electrolysis and the Ions.*—These experiments were carried out with the object of ascertaining whether the colour of the solutions was due to the positive or negative ions. The method adopted was that of Masson (*Phil. Trans.*, 1899, **192**, [*A*], 331), a solution of the pure salt in both the anode and the cathode compartments being used, and a joining tube containing potassium chloride in gelatin.

(*a*) *Neutral Ammonium α-Compound.*—Copper tartrate was deposited at the anode and a gas evolved. At the cathode, copper was deposited and ammonia evolved. A blue anion appeared in the connecting tube; after a time a darker blue anion also appeared (probably due to the formation of Schiff's salt in the cathode compartment by interaction with the ammonia there liberated). The precipitates of copper and copper tartrate are due to secondary actions, but the liberation of ammonia is to be expected if ammonium is the positive radicle of the salt. There was no appearance of a blue cation in the connecting tube.

(*b*) *Alkaline Compound.*—If the solution obtained by dissolving copper tartrate in excess of ammonia be electrolysed in the apparatus described, a dark blue positive ion travels down the tube and a violet-blue negative ion moves in the opposite direction. This confirms the equation given, at least qualitatively, for the production of the alkaline from the neutral compound, when both a blue positive ion, $Cu(NH_3)_4^{\cdot\cdot}$, and a violet-blue negative ion are formed.

With a solution of the pure alkaline ammonium compound no coloured positive ion is produced, but in the anode compartment the solution gradually becomes neutral and its colour changes to that of the neutral α-compound, when copper tartrate is deposited on the anode and gassing occurs. At the cathode, copper is deposited and some ammonia evolved. The production of copper is due to reduction at the cathode.

C. *Alkaline Alkali-metal Compounds.*

A very large number exists, but they are as a rule very unstable, instability increasing with alkali content. All are able to oxidise glucose. These alkaline solutions behave differently on boiling, according to the proportion of alkali they contain. With small amounts of alkali the solutions precipitate cuprous oxide and change in colour, but with larger amounts of alkali boiling for a short time does not produce any apparent change.

(1) *Sodium Cupritartrate-B.*—Masson and Steele at the end of

their paper mention a compound in which the atomic ratio Na : Cu=7 : 4.

When copper tartrate is dissolved in sodium hydroxide solution in the proportion $2NaOH : CuC_4H_4O_6$, and 90 per cent. alcohol added to the deep blue solution, separation into two layers occurs. The lower oily layer is blue and contains the complex salt. On rubbing this layer with successive small quantities of absolute alcohol, it gradually thickens, and when all the water is extracted, finally crystallises. For analysis, the oily material was washed with 60 per cent. alcohol until the washings were neutral, dissolved in water, reprecipitated, and crystallised as described above. The crystals were washed with absolute alcohol and ether, and quickly dried in the air at 25° (Found: Na=12·92; Cu=20·34; C=15·17; H=3·24. $7NaOH,4CuC_4H_4O_6,7H_2O$ requires Na=12·86; Cu=20·30; C=15·33; H=2·98 per cent.). In the air this salt readily absorbs carbon dioxide and moisture.

The crystals are exceedingly hygroscopic and readily decompose in the air with the production of a green, oily substance which sets to a green, enamel-like solid. On heating at 100°, or even at the ordinary temperature, the crystals decompose.

(2) An attempt was made to prepare the corresponding potassium salt, but a compound (Cu=21·92; K=10·70 per cent.) was obtained which gave results corresponding with the formula $K_4Cu_5C_{16}H_{52}O_{45}$ or $4KOH,4CuC_4H_4O_6,Cu(OH)_2,15H_2O$.

(3) A more alkaline compound was obtained by dissolving copper tartrate in sodium hydroxide solution in the proportion $CuC_4H_4O_6 : 6NaOH$, and treating the solution as described under sodium cupritartrate-B. It was a deeper blue in colour, and decomposed more readily than the less alkaline compound. Decomposition at the ordinary temperature was quite marked after a week or so. The solution, however, was stable on boiling, but readily oxidised glucose (Found: Na=17·20; Cu=16·75; C=14·10; H=3·34 per cent. These figures agree well with a somewhat complex formula, $Na_{23}Cu_8C_{36}H_{95}O_{94}$).

D. Attempt to Isolate the Blue Complex.

Copper tartrate dissolves readily in a solution of Rochelle salt, sodium tartrate, or potassium tartrate. Ninety per cent. alcohol causes a separation into two layers, the lower being dark blue. Colourless crystals of alkali-metal tartrate were readily deposited from this oily layer, especially on treatment with alcohol. By a series of fractional precipitations of this oily layer from aqueous solution by alcohol, an attempt was made to obtain the blue complex free from alkali-metal tartrate, but on crystallisation of the purified oil in a desiccator, only crystals of alkali-metal tartrate, coloured in places by the complex, were obtained.

The solutions all showed a marked tendency to deposit cuprous oxide, and were originally feebly acid, but after purification became neutral.

The dark blue complex here encountered is apparently stable only in the presence of a high concentration of alkali-metal tartrate.

It is of interest to note that barium tartrate also is soluble in solutions of sodium or potassium tartrate.

Summary.

The following compounds have been described and analysed.

I. Neutral α-Cupritartrates.

(1) Sodium α-cupritartrate, $Na_3Cu_4C_{12}H_9O_{19},11H_2O$.

(2) Barium α-cupritartrate, $Ba_3(Cu_4C_{12}H_9O_{19})_2,27H_2O$.

(3) Ammonium α-cupritartrate, $(NH_4)_3Cu_4C_{12}H_9O_{19},9H_2O$.

These correspond with Masson and Steele's potassium, silver, and lead salts.

II. Alkaline Alkali-metal Compounds.

(1) The sodium compound, $4CuC_4H_4O_6,7NaOH,7H_2O$, obtained by dissolving copper tartrate in sodium hydroxide solution in the proportion $CuC_4H_4O_6 : 2NaOH$.

(2) A potassium compound, using the same synthetic proportions as in (1), yet yielding the atomic ratio $K : Cu = 4 : 5$.

(3) A more alkaline sodium compound by dissolving copper tartrate in sodium hydroxide solution in the proportion

$$CuC_4H_4O_6 : 6NaOH.$$

III. Ammonium Compounds.

(1) Neutral α-cupritartrate. See under I.

(2) Neutral ammonium β-cupritartrate, $(NH_4)_2Cu_3C_8H_6O_{13},6H_2O$.

(3) Alkaline ammonium compound, $Cu(NH_3)_4C_4H_4O_6,H_2O$, or $(NH_4)_2CuC_4H_4O_7,2NH_3$ (Schiff's salt).

The following empirical mode of formulation shows the relationship between these compounds. Water of crystallisation is omitted.

$$\begin{array}{ll} \left.\begin{array}{ll} (NH_4)_2Cu_3C_8H_6O_{13} & \equiv 2(CuNH_4H_3C_4O_6),CuO \\ (NH_4)_3Cu_4C_{12}H_9O_{19} & \equiv 3(CuNH_4H_3C_4O_6),CuO \\ Na_3Cu_4C_{12}H_9O_{19} & \equiv 3(CuNaH_3C_4O_6),CuO \end{array}\right\} & \text{neutral.} \\ \begin{array}{ll} K_4Cu_5C_{16}H_{12}O_{25} & \equiv 4(CuKH_3C_4O_6),CuO \\ Cu(NH_3)_4C_4H_4O_6 & \equiv Cu(NH_4)_4C_4O_6. \end{array} & \end{array}$$

The subject of this research was suggested to us by Professor Masson, to whom we are further indebted for much valuable advice and assistance.

UNIVERSITY OF MELBOURNE. [*Received, May 9th,* 1921.]

CLV.—*The Labile Nature of the Halogen Atoms in Substituted Nitromethanes.*

By ALEXANDER KILLEN MACBETH and DAVID DOIG PRATT.

BALY AND COLLIE (T., 1905, **87**, 1332) showed that the introduction of a nitro-group into the benzene nucleus brought about a complete change in the vibration of the benzene molecule. It is therefore not surprising to find marked abnormalities in chemical properties in the case of aromatic nitro-compounds. This is very pronounced in the case of the polynitro-compounds, and especially in those substances where the disposition of the nitro-groups is such as to allow them to exert a joint ortho-para-influence. In picryl chloride, for example, such a structure is present and is characterised by the extreme lability of the halogen atom, which is replaced by an amino-group by the action of ammonia.

The chemical nature of the polynitro-compounds has been studied by examining their behaviour on treatment with hydrazine. Rothenburg (*Ber.*, 1893, **26**, 2060) first pointed out that hydrazine reduced the simple aromatic nitro-compounds to the corresponding amines. Curtius and his co-workers (*J. pr. Chem.*, 1907, [ii], **76**, 233, 281, 301) gave further examples of the same kind and showed that in the case of the dinitro-compounds one only of the groups was reduced. Giua (*Gazzetta*, 1919, **49**, [ii], 146, 152, 166) has examined the effect of hydrazine on trinitro-aromatic compounds in which the nitro-groups exert an ortho-para-influence. In such cases replacement of the labile group occurs with the formation of substituted hydrazines. A similar effect has been observed by Purgotti (*Gazzetta*, 1894, **24**, [i], 112), who found that on boiling a mixture of hydrazine sulphate and potassium hydroxide with picryl chloride in alcoholic solution crystals of picryl hydrazide result.

It was thought that alkaline hydrazine solutions should prove useful in studying the chemical nature of the substituted nitromethanes, more especially with a view to examine the reactivity of the halogen atom in the halogen derivatives. In the case of tetranitromethane it was found by one of us (T., 1920, **117**, 880) that, as in the case of the trinitro-aromatic compounds, no reduction of the nitro-groups to amino-groups occurred on treatment with alkaline hydrazine, but one of the nitro-groups was removed, the potassium salt of nitroform being produced. The reaction takes place quantitatively, as measurements of the liberated nitrogen are in agreement with the equation :

$$2C(NO_2)_4+N_2H_4+4KOH=2(NO_2)_3CK+2KNO_2+N_2+4H_2O.$$

The action of hydrazine has been extended to the case of other substituted nitromethanes and the results are now recorded. Chlorotrinitromethane, bromotrinitromethane, bromodinitromethane, dibromodinitromethane, trichloronitromethane, phenylbromodinitromethane, and bromonitromethane have been examined, and, with the exception of the last compound, all these substances readily oxidise hydrazine in alkaline solution with the liberation of nitrogen at the ordinary temperature. The reaction is in all cases quantitative and may be used to estimate the amounts of the different nitro-compounds present in solution. In the estimations a van Slyke nitrometer (*J. Biol. Chem.*, 1912, **12**, 278) was used and was found to be much more convenient than the method previously described (*loc. cit.*).

Chlorotrinitromethane.—This was prepared by the method outlined by us (this vol., p. 354). Ten c.c. of an alcoholic solution containing 10·0558 grams per 100 c.c. were introduced into the deaminising bulb of the nitrometer and 10 c.c. of a freshly prepared, alkaline solution of hydrazine were then added. The latter solution is conveniently prepared by dissolving 10 grams of hydrazine sulphate in 80 c.c. of hot water and adding 20 grams of potassium hydroxide. After cooling and filtering, the solution is diluted to 100 c.c. Nitrogen is quickly evolved when the chloronitroform is treated with this solution, the reaction proceeding according to the equation:

$$2C(NO_2)_3Cl+N_2H_4+4KOH=2(NO_2)_3CK+2KCl+N_2+4H_2O.$$

A series of estimations with the above solutions gave values of 10·03, 10·05, 10·00, and 10·12 grams of chloronitroform per 100 c.c. The salt precipitated during the reaction was collected and examined. After recrystallisation, it gave a result too low for the potassium content of the salt of nitroform, and so is probably a mixture of the potassium and hydrazine salts. After acidifying an aqueous solution of the salt and extracting with ether, the potassium salt of nitroform was isolated by adding alcoholic potassium hydroxide to the ethereal extract (Found: K=20·5. Calc., K=20·64 per cent.). It is therefore apparent that the halogen atom in chlorotrinitromethane is labile, being easily removed by hydrazine reduction. The equation of the reaction established above shows that in this case there is no reduction of the nitro-groups to amino-groups, the substance behaving chemically like the polynitro-aromatic compounds, in which the groups exert the ortho-para-influence.

Bromotrinitromethane.—This substance was prepared by the method described by us (this vol., p. 354). A very pure sample was obtained by the action of bromine on a solution of nitroform in nitric acid. The crude bromo-compound was washed with a dilute solution of sulphurous acid to remove the excess of bromine. It was then extracted with ether and the extract dried with sodium sulphate. On distilling over silver carbonate under reduced pressure, the bromonitroform solidified in the condenser. An alcoholic solution containing 10·5321 grams per 100 c.c. was prepared for use in the van Slyke nitrometer, and the estimation of the nitrogen liberated by hydrazine was carried out as described in the previous section. A series of observations gave 10·514, 10·460, and 10·532 grams of bromo-compound per 100 c.c. The errors are therefore respectively 0·172, 0·712, and 0·008 gram per litre of solution. The results were calculated on the basis of the equation :

$$2C(NO_2)_3Br+N_2H_4+4KOH=2(NO_2)_3CK+2KBr+N_2+4H_2O.$$

The salt precipitated in the reaction was treated as in the case of the chloro-compound, and the potassium salt of nitroform was isolated (Found: K=20·7. Calc., K=20·64 per cent.). The reduction proceeds rapidly in this case also and the reaction shows that the halogen atom is easily removable by hydrazine, but no reduction of nitro- to amino-groups takes place. This reaction provides a very good method for controlling the purity of bromonitroform.

Dibromodinitromethane.—This was prepared from tribromoaniline and purified by shaking with aqueous potassium hydroxide solution to form the potassium salt of monobromodinitromethane. On dissolving this in water, acidifying with dilute sulphuric acid and distilling in steam, fairly pure dibromodinitromethane is collected. A purer specimen is obtained by extracting the distillate with ether, dehydrating the extract with sodium sulphate, and distilling under reduced pressure. The pure compound distils at 76—77°/14 mm. It may be mentioned, however, that in many cases the vacuum distillation is unsuccessful, decomposition taking place. Hydrazine liberates nitrogen quantitatively, one bromine atom being removed in the cold according to the equation :

$$2CBr_2(NO_2)_2+N_2H_4+4KOH=2(NO_2)_2CKBr+N_2+2KBr+4H_2O.$$

No reduction of the nitro-groups takes place, and the bromine atom is removed with ease; the second bromine atom is removed by the action of hydrazine at higher temperatures. Other reducing agents have a similar effect, breaking down the compound to dinitromethane (compare Duden, *Ber.*, 1893, **26**, 3004).

Chloropicrin.—This compound is only attacked very slowly by alkaline solutions of hydrazine, one of the chlorine atoms being removed. A sample of chloropicrin was distilled under reduced pressure, and an alcoholic solution prepared containing 10·1474 grams per 100 c.c. In different experiments, 5 c.c. of this solution liberated nitrogen as follows: 36·9 c.c. at 13·5° and 762 mm.; 36·8 c.c. at 13·4° and 760 mm.; 36·8 c.c. at 13° and 760 mm. These results give an average value of 14·023 grams of nitrogen liberated from hydrazine by the gram-molecule of chloropicrin. The reaction therefore proceeds according to the equation:

$$2CCl_3{\cdot}NO_2+N_2H_4+4KOH=2CCl_2K{\cdot}NO_2+2KCl+N_2+4H_2O.$$

The reaction takes place slowly, the evolution of nitrogen extending over two or three hours at the ordinary temperature. The quality of the chloropicrin has a great effect on the reaction, but a sample freshly distilled under reduced pressure gives quantitative results. It will be seen that in this case the halogen atoms are not nearly so labile as in the substances previously studied, and this may justly be attributed to the fact that only one nitro-group is present in the molecule.

Bromonitromethane.—In the previous case, although only one nitro-group is present in the molecule, it is accompanied by the three strongly electronegative chlorine atoms, and the joint action of these may possibly be responsible for the labile nature of the removable halogen atom. In the case of monobromonitromethane, this possibility is excluded and it was thought of interest to examine its behaviour on treatment with hydrazine. As a result of our work we are of opinion that this substance is best prepared by Scholl's method (*Ber.*, 1896, **29**, 1824), the method of Tscherniac (*Ber.*, 1895, **30**, 2588) giving very uncertain results. At the ordinary temperature, hydrazine is without action on monobromonitromethane, but the halogen atom appears to be removed by this agent at higher temperatures. Thus, in one experiment the bromo-compound was refluxed with alkaline hydrazine solution for half an hour, and after cooling and acidifying with dilute sulphuric acid the mixture was steam-distilled. The distillate was extracted with ether and the extract dehydrated by standing for some time over sodium sulphate. On distillation, a little oil was collected at 100°, which had a refractive index 1·3935. This appears to be nitromethane (b. p. 100°; $n=1{\cdot}39348$).

Phenylbromodinitromethane.—This was prepared from benzaldoxime. The action of nitrogen peroxide converts this into phenyldinitromethane (Ponzio, *J. pr. Chem.*, 1906, [ii], **73**, 494). This is converted into the sodium salt by dissolving 9·2 grams in 100 c.c. of alcohol and adding 1·5 grams of sodium dissolved in 50 c.c. of alcohol. During the addition the mixture is kept cool and stirred vigorously. The salt is filtered with the aid of the pump, washed with ether, and dried in a vacuum desiccator. The dry salt is added slowly to a solution of 8 grams of bromine in carbon disulphide, the whole being cooled in ice. When all the salt has been added, the mixture is allowed to stand for half an hour, after which it is washed with a little water to remove sodium bromide, and then with a dilute solution of sulphurous acid to remove the excess of bromine. After drying, the carbon disulphide is distilled off and phenylbromodinitromethane remains. It does not distil at 100°/15 mm., but shows signs of decomposing. Accordingly the crude phenyl bromodinitromethane is subjected to steam distillation, when it comes over slowly. A white, crystalline substance remains in the flask. This is soluble in hot water, melts at 113° and apparently contains no bromine. It has not been further examined.

Phenylbromodinitromethane is a pale yellow oil, which is insoluble in water and has a refractive index $n=1{\cdot}5650$ (Found: Br=30·24. Calc., Br=30·6 per cent.). It is broken down by alcoholic potassium hydroxide, the potassium salt of phenyldinitromethane being formed according to the equation:

$$3C_6H_5{\cdot}CBr(NO_2)_2+6KOH= \\ 3C_6H_5{\cdot}CK(NO_2)_2+2KBr+KBrO_3+3H_2O.$$

On treatment with an alkaline solution of hydrazine, phenyl bromodinitromethane is rapidly reduced, nitrogen being liberated. An alcoholic solution containing 5·3472 grams of the bromo-compound was prepared for use in the van Slyke nitrometer. In a series of estimations, 10 c.c. of this solution, on treatment with hydrazine, liberated an average volume of 24·8 c.c. of nitrogen at 12° and 752 mm. This corresponds with 14·04 grams of nitrogen for the gram-molecular quantity of phenylbromodinitromethane. The reaction is therefore expressed by the equation:

$$2C_6H_5{\cdot}CBr(NO_2)_2+N_2H_4+4KOH= \\ 2C_6H_5{\cdot}CK(NO_2)_2+2KBr+N_2+4H_2O.$$

The salt precipitated during the estimations was collected and examined. Part of it was dissolved in water, the solution acidified with sulphuric acid, and extracted with ether. The potassium salt of phenyldinitromethane was obtained from the ethereal extract on the addition of potassium ethoxide (Found: K=17·9. Calc., K=17·73 per cent.). Another part of the ethereal extract was washed with a little dilute sodium hydroxide solution and the ether removed by bubbling air through the solution for some time. On acidifying the solution, phenyldinitromethane separated as a white solid melting at 79°. It may therefore be assumed that in this case also the hydrazine readily removes the halogen atom without any reduction of the nitro-group.

From the results recorded it is seen that the presence of nitro-groups in the halogen derivatives of methane renders the halogen atom more labile than it is in the case of the alkyl haloids. The effect is more pronounced when several nitro-groups are present, since the di- and tri-nitrobromomethanes part with their bromine in the cold, whereas bromonitromethane is only broken down to nitromethane on heating. The presence of other electronegative atoms or groups enhances the effect of the nitro-groups, as chloropicrin parts with one of its chlorine atoms at the ordinary temperature, in contradistinction to bromonitromethane. This effect is further exemplified by the cases of phenylbromodinitromethane and dibromodinitromethane. The latter substance parts with one of its bromine atoms at the ordinary temperature, forming the salt of monobromodinitromethane, which is not further attacked; whereas the halogen atom is readily removed from phenylbromodinitromethane at the ordinary temperature in virtue of the electronegative phenyl group reinforcing the action of the nitro-groups. A certain parallel may be drawn between the behaviour of the polynitro-aliphatic compounds and the polynitro-aromatic substances, especially those in which the ortho-para-influence of the nitro-groups exists; in neither case does reduction of the nitro-group to an amino-group occur, but in both replacements take place.

The effect of the nitro-group in increasing the lability of halogens in the aliphatic series becomes more marked when the action of hydrazine on such substances is contrasted with the negative results obtained in the case of other halogen derivatives. Thus, no liberation of nitrogen at the ordinary temperature is noted when hydrazine is added to solutions of chloroacetone, glycerol, monochlorohydrin, or dichlorohydrin, ethyl chloroformate, chloromethyl acetate, chloromethyl ether, bromoacetic acid, trichloroacetic acid and other substances of a like nature.

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CLVI.—*Colorations produced by Substituted Nitroforms.*

By HUGH GRAHAM and ALEXANDER KILLEN MACBETH.

IN previous papers (T., 1915, **107**, 87, 1824) the colorations produced by the interaction of tetranitromethane and other substances were discussed, and an explanation based on the spectrographic study of the different cases was advanced. From an examination of the different absorption curves it was found that the general effect obtained on mixing tetranitromethane and a substance containing either an ethylene linking or an atom capable of exercising a higher valency was the development of a strong selective absorption with a maximum in the region $1/\lambda$ 2850. This absorption band bears a very strong resemblance to that noted in the case of some poly-nitro-aliphatic compounds, to which Hantzsch and Voight (*Ber.*, 1912, **45**, 85) ascribed the conjugated *aci*-nitro-structure. As tetranitromethane does not contain the hydrogen atom necessary for the intramolecular change involved in the formation of such a grouping, the conjugated *aci*-structure was deemed inapplicable in this case; and since the organic nitrites were found to develop colours similar to those observed with tetranitromethane under the same conditions, a hypothesis, which postulated a change in structure from a nitro- to a nitrite group, was advanced to account for the behaviour of the latter substance. This view was supported by the similarity between the absorption band characteristic of the organic nitrites and that developed in the solutions of tetranitromethane. Later, Schmidt (*Ber.*, 1919, **52**, [*B*], 400), as a result of his study of the behaviour of tetranitromethane on treatment with alkali, concluded that the compound in some cases reacts as if it contained a nitrite group, but his reference to the fact that we had previously indicated this is conspicuous by its absence.

Macbeth and Pratt (this vol., p. 354) prepared the chloro- and bromo-derivatives of nitroform and showed that these gave a series of colours with substances which react with tetranitromethane. It seemed likely that a spectrographic examination of these cases might throw further light on the question of colour production, and the results are now recorded. As dibromodinitromethane gives faint colorations with some compounds, it was also examined.

The method of study adopted was essentially the same as that described in a former paper (*loc. cit.*), and the results obtained are expressed in the accompanying figures. Alcoholic solutions containing the nitro-compounds and different influencing substances were examined and their absorptions recorded. Piperidine, methylamine, carvene, diethyl sulphide, ethyl mercaptan, and pentamethylene sulphide were selected as representative influencing substances. The amounts of these added to the solutions of the nitro-compounds were such as to be practically diactinic, and thus

FIG. 1.

———————— *Bromonitroform in alcohol.*
— . — . — . ,, *in chloroform.*
— . . — . . — *Tetranitromethane + pentamethylene sulphide.*
——— . . . . ——— ,, *+ methylamine (after mixing).*
. . . . *Bromonitroform + piperidine (after mixing).*

FIG. 2.

— . . — . . — *Chloronitroform in chloroform.*
———————— ,, *in alcohol.*
. . . . *Dibromodinitromethane in alcohol.*
——— . . . . ——— ,, *in piperidine.*
— — — — — — *Potassium salt of monobromodinitromethane in water.*

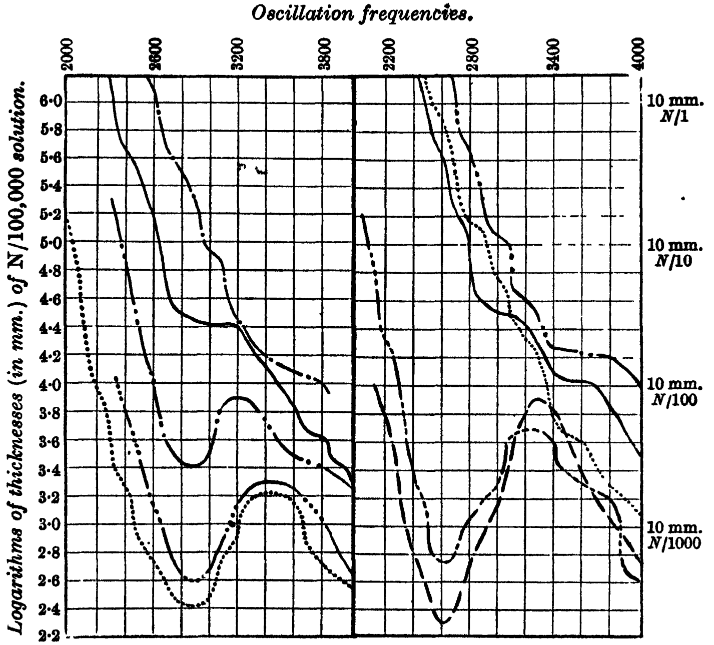


FIG. 1. FIG. 2.

in no way interfere with the absorption of the latter unless chemical action had taken place.

The absorption curves of bromotrinitromethane in chloroform and in alcohol are shown in Fig. 1. The graphs of the corresponding chloro-compound are given in Fig. 2. It will be noted that these substances show general absorption only, the curves being characterised by a number of "kicks." In the case of the bromo-compound in alcohol, it will be seen that there is a marked kick or shallow band in the region 1/λ 2800—1/λ 3200, and as this is the position in which the band characteristic of the conjugated *aci*-form of aliphatic compounds appears, it seems probable that in alcoholic solution bromonitroform exists to some extent in this form. It would therefore appear that the bromine atom in this compound is capable of wandering from the carbon atom to give the tautomeric conjugated *aci*-form. A similar effect, but of smaller degree, is seen in the case of the alcoholic solution of the chloro-compound.

Piperidine, when added to solutions of any of the above nitro-compounds, immediately produces a pronounced yellow colour, and the absorption of the substances undergoes a radical change. The effect of the base is seen in the different figures. In the case of dibromodinitromethane the absorption curve now shows a deep band with a maximum in the region 1/λ 2600. The bands in the case of the chloro- and bromo-nitroforms are in the region 1/λ 2800—1/λ 3000, and it will be seen that there is a marked similarity between these curves and that obtained when tetranitromethane is mixed with methylamine (Fig. 1).

In seeking an interpretation of these curves it will be observed that they bear a great resemblance to that characteristic of the conjugated *aci*-form of trinitromethane (Hantzsch, *loc. cit.*). Reference to the graphs of chloro- and bromo-nitroform shows that although there is an indication that these may exist to some extent in the conjugated *aci*-form in alcoholic solutions, yet the amount of such type present must be very small and can only be responsible for slight selective absorption of the conjugated *aci*-type. It seems unlikely that the presence of piperidine merely exerts an influence to induce a further intramolecular change into the conjugated *aci*-structure. Moreover, it has been shown that the halogen atoms in chloro- and bromo-nitroform are labile (Macbeth and Pratt, this vol., p. 1357), and that one of the nitro-groups of tetranitromethane is readily split off by hydrazine (T., 1920, **117**, 880). In these cases, *aci*-salts of nitroform were isolated, and it is probable that such an elimination occurs in the presence of organic bases, with the formation of the piperidine, or other, salt of nitroform. The salts of nitroform all absorb light strongly, and their absorption curves are characterised by a powerful selective effect in the region 1/λ 2800—1/λ 3000. The curve of an aqueous solution of the potassium salt of nitroform is given in Fig. 4, and it will be seen that this is of the same type as the absorption curves of chloro-

and bromo-nitroform in the presence of piperidine (dotted curves, Figs. 1, 3, 4). The absorption of tetranitromethane in the presence

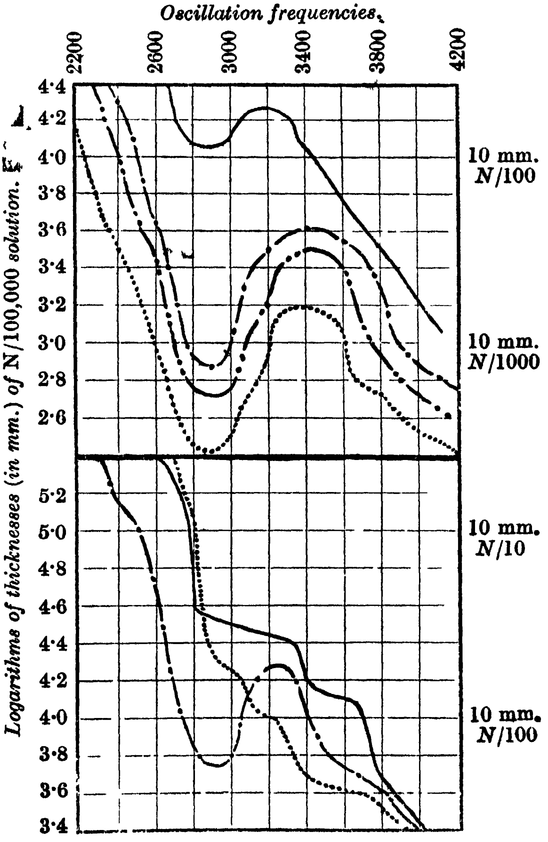
FIG. 3.

Upper curves.

———————— *Chloronitroform* + *carvene* (*after* 15 *hours*).
— . — . — „ + *mercaptan* (*after* 1 *hour*).
— .. — .. — „ + *ethyl sulphide* (*after* 3 *hours*).
. . . . „ + *piperidine*.

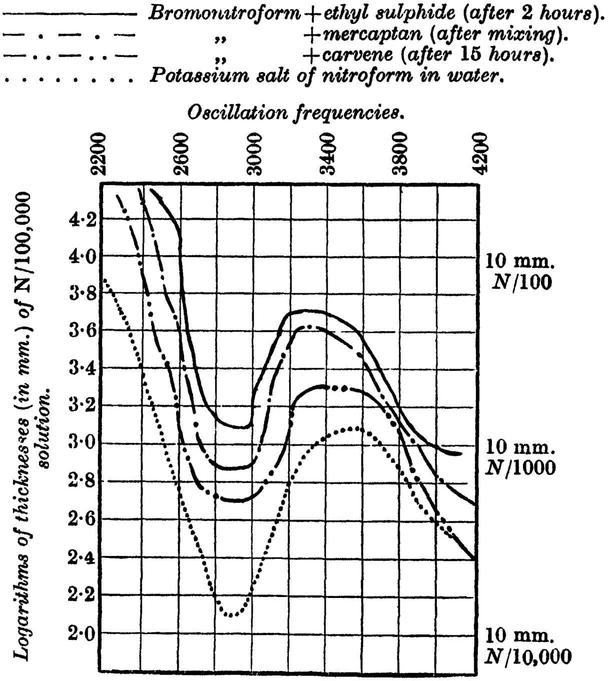
Lower curves.

———————— *Dibromodinitromethane* + *ethyl sulphide* (*after* 24 *hours*).
. — . — . — „ + *carvene* (*after* 3 *days*).
. . . . „ + *mercaptan*.



of methylamine closely resembles the above curves, and therefore it is probable that in all these cases the selective effect is due to the same cause. There seems to be, therefore, strong grounds for supposing that the colours produced when piperidine and other organic bases react with chloro- and bromo-nitroform and with tetranitromethane are due to the breakdown of these substances to the piperidine and other salts of nitroform which have the conjugated *aci*-structure. This view seems the more plausible since it has been shown that the halogen atoms and the fourth nitro-group are readily eliminated from nitroform derivatives. This may be regarded as the first step in the change which leads to the colorations due to the conjugated *aci*-salts.

FIG. 4.



If this view is correct, similar considerations should hold in the case of dibromodinitromethane. It has been shown (Macbeth and Pratt, this vol., p. 1358) that one of the bromine atoms in this substance is labile, and the action of piperidine may consist in the removal of this atom with the formation of the coloured salt of monobromodinitromethane. This is supported by an examination of the absorption of the potassium salt of the latter, which is found closely to resemble that of dibromodinitromethane in the presence of piperidine. Both curves show a deep absorption band with its maximum at about 1/λ 2600 (Fig. 2).

Other influencing substances, such as carvene, ethyl mercaptan, and the organic sulphides, produce effects similar to those of the organic bases when they act on tetranitromethane and the halogen derivatives of nitroform. As a rule, however, the action is much slower in these cases. Thus, with the sulphides some three hours elapse before the selective absorption becomes very marked, and with carvene and other unsaturated compounds considerably longer intervals are necessary. It is probable that the breakdown to nitroform occurs in these cases also, and that the colorations observed are due to the absorbing variety of the derivative of this compound. All the compounds which give rise to colour are susceptible to oxidation and may therefore reduce the several nitro-compounds. The different times required in the various cases are doubtless connected with the readiness with which the influencing substances undergo oxidation, as the formation of the corresponding nitroform derivatives is directly dependent on this action. If the hypothesis is correct, one would expect to find a gradual decrease in the amounts of tetranitromethane and the nitroform halogen compounds present in solutions containing influencing substances. A ready method of estimating the amounts of these nitro-compounds is at hand in the hydrazine reaction, and investigations are being undertaken with this in view. It may be mentioned that preliminary estimations show the expected fall off in the amounts of the different nitro-compounds, and the hypothesis put forward above to account for the colorations therefore gains considerable support.

That there is a marked difference in the reactivity of the different nitro-compounds is seen by a reference to the curves. Thus chlorotrinitromethane is not attacked by carvene to the same extent as the bromo-compound, since in the former case the band penetrates only to about 10 mm. of an *N*/100-solution, whilst in the latter it is found in the *N*/10,000-solution.

The colours obtained with dibromodinitromethane and the different influencing substances—with the exception of piperidine—are very faint. It may reasonably be concluded that, apart from the cases of the organic bases, this nitro-compound is but slowly reduced; and since only small amounts of the corresponding derivative of monobromodinitromethane are accordingly produced, there can be little formation of the conjugated *aci*-type which is responsible for the strong selective absorption. The colorations—apart from the bases—are therefore faint. Reference to Fig. 3 (lower curves) will show that with carvene a weak selective absorption is developed only after three days; with ethyl sulphide, a kick (which may be regarded as a very shallow band) is the only effect produced after twenty-four hours' interaction.

It seems reasonable to suppose that the colorations observed when the polynitromethanes are acted on by organic bases or substances containing either ethylene linkings or atoms capable of exercising a higher valency are due to the reduction of the nitro-compound to nitroform derivatives which exist in the conjugated *aci*-form. On this hypothesis, it has not been necessary 'to inquire into the structure of conjugated *aci*-compounds. Hantzsch (*loc. cit.*) proposes formulæ in which a special type of six-membered ring is present. The structure comprises different classes of compounds, the criterion of the conjugated *aci*-structure being the development of a strong selective absorption in the derivatives of a substance which itself shows only general absorption, or at the most a very weak selective effect. The maxima of the bands vary in the different classes, but in the case of the trinitro-compounds of the type with which we are dealing the bands are all found in the same region, having a maximum at or about $1/\lambda$ 2800—$1/\lambda$ 3200. Whether the structure Hantzsch proposes for the conjugated *aci*-compounds is correct or not is an open question, but it seems to us that the connexion between these substances and the organic nitrites cannot be overlooked. In both cases the maximum of the selective absorption is in the same region of frequency; and the nitrites, moreover, are capable of colour production on treatment with appropriate substances. The change in structure which gives rise to conjugated *aci*-trinitro-compounds probably results, in our opinion, in a linking of the nitro-groups akin to that occurring in the nitrites.

We wish to express our thanks to Professor A. W. Stewart and the Queen's University of Belfast for access to their spectroscope; to Mr. D. D. Pratt for assistance in the preparation of some of the materials used in this work, and to Mr. D. T. Gibson for help in the photographic work.

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CLVII.—*The Hydration of the Fibres of Soap Curd. Part I. The Degree of Hydration determined in Experiments on Sorption and Salting Out.*

By JAMES WILLIAM McBAIN and HERBERT ERNEST MARTIN.

IN recent communications from this laboratory it has been shown that soap curds consist of a felt of microscopic or ultramicroscopic fibres of hydrated neutral soap enmeshing sols or gels of soap or solutions of any electrolyte present.

In a previous communication (T., 1919, **115**, 1300) an attempt was made to determine the degree of hydration of the soap which forms the curd fibres. The method was based on the observation that when soap is salted out in the presence of free sodium hydroxide the concentration of the latter is thereby increased. This can be explained as being due to hydration of the curd fibres, which abstracts some of the solvent from solution, and on making the further assumption that no sodium hydroxide is sorbed by the fibres, a quantitative estimate of their hydration was afforded. The experimental difficulties involved in the use of sodium hydroxide for this purpose are, however, not inconsiderable, and it was desirable to find some more suitable reference substance.

Whereas previously the sodium hydroxide had served both as agent for salting out and as reference substance, the attempt was now made to use a small quantity of an easily analysed electrolyte as reference substance in the presence of a large amount of another electrolyte used to salt out the soap. Sodium sulphate was found to be fairly satisfactory, but only in the presence of a concentrated solution of another salt.

EXPERIMENTAL.

The soap systems, mixtures of curd with excess of mother-liquor, were all prepared in tubes of pure silver in the manner described by McBain and Taylor (*Zeitsch. physikal. Chem.*, 1911, **76**, 199). They were shaken for many weeks at temperatures between 90° and 100° in the hope of ensuring complete reaction, and then placed in a thermostat at 30° for a few days in order that the hydration should adjust itself to this temperature. However, six years later, Miss Laing (T., 1920, **117**, 1506) showed that the solubility of the curd fibres requires weeks or months to adjust itself completely to changed conditions, so that the results here described probably refer in some cases to a temperature considerably above 30°. This, however, as we now know, cannot influence the degree of hydration by more than 10 per cent. as a maximum.

In some cases the curd was made by adding together palmitic acid, sodium hydroxide solution, sodium chloride, and water in calculated amounts, but it was found that local incrustations with hard curd prevented interaction in the time allowed. This was finally avoided by first making up the solution of sodium palmitate and afterwards salting it out and leaving it during several weeks at 90°. In all cases, Kahlbaum's purest materials and sodium hydroxide from sodium drippings, free from carbon dioxide, were employed. Upon opening the tube the contents were filtered through silver gauze at 30°, the filtrate being referred to throughout this paper as mother-liquor. Specimens of both mother-liquor and curd wet with mother-liquor were submitted to complete analysis, the chloride and sulphate being estimated gravimetrically as silver chloride and barium sulphate respectively. A number of different procedures were employed for this purpose, and in some cases separate samples were used for the different estimations; water was always estimated by difference. The method of calculation of the hydration has previously been described (*loc. cit.*).

The data of the experiments in which 1·0*N*-sodium palmitate was salted out by saturated or nearly saturated sodium chloride solution in the presence of a small amount of sodium sulphate are given in Table I. Two experiments in which 1·0*N*-sodium palmitate was salted out by 2·0*N*-sodium hydroxide in the presence of a small quantity of sodium chloride are recorded in Table II. Two experiments in which the sodium chloride was only one-third saturated and sodium sulphate was used as reference substance are given in Table III; here the composition of the mother-liquor and the hydration of the curd were deduced from the analysis and total weight of the curd.

TABLE I.

No. of expt.	Original charge 1·0*N*-NaP. Grams per 100 grams of H_2O		Mother-liquor analysis. Grams per 100 grams of H_2O			Hydration. Mols. H_2O to 1NaP.	
	NaCl.	Na_2SO_4.	NaCl.	Na_2SO_4	NaOH.	NaCl.	Na_2SO_4.
7	33·49	1·84	33·59	1·914	0·0104N	0·17	2·14
8	32·73	1·82	33·06	1·881	0·0033N	0·55	1·79
11	32·62	1·250	33·18	1·309	0·0022N	0·96	2·49
13	24·08	1·897	24·35	1·954	0·0135N	0·63	1·62
15	24·08	1·897	(23·27) ?	1·962	0·0021N	?	1·83

TABLE II.

No. of expt.	Charge 1·0N-NaP. Grams per 100 grams of H_2O		Mother-liquor. Grams per 100 grams of H_2O				Hydration. Mols. H_2O to 1NaP.	
	NaCl.	NaOH.	NaCl.			NaOH.	NaCl.	NaOH.
4	2·018	8·058	2·089			8·221	1·90	1·37
18	4·185	8·005	4·298			7·818	1·47	—
			Curd compositions. Grams per 100 grams of curd.					
				NaP.	H_2O.			
18	4·185	8·005	2·199	37·71	53·99	4·105	0·9	1·7
			2·077	41·75	52·32	3·854	1·5	2·2

TABLE III.

No. of expt.	Charge 1·0N-NaP. Grams per 100 grams of H_2O.		Curd composition. Grams per 100 grams of curd.				Hydration. Mols. H_2O to 1NaP.	
	NaCl.	Na_2SO_4.	NaCl.	Na_2SO_4.	NaP.	H_2O.	NaCl.	NaOH.
16	11·68	2·245	4·917	0·8702	46·45	47·76	2·54	3·94
			4·998	0·9074	45·37	48·72	2·71	3·80
17	11·68	2·245	5·248	1·060	42·48	51·21	3·27	2·09
			5·297	1·041	41·03	52·63	3·9	3·41

Discussion of the Results.

(*a*) *Hydrolysis of Soap on Salting Out.*

It will be seen from Experiments 8, 11, 15, 16, and 17 that when a normal solution of neutral sodium palmitate is salted out with sodium chloride of concentrations ranging from one-third to complete saturation, the mother-liquor is alkaline to the extent of only 0·002—0·004N-sodium hydroxide. In other words, soap salted out with neutral sodium chloride contains an amount of sodium which is within 99·6—99·8 per cent. of that required exactly to neutralise the fatty acid present. Practical soap-boilers frequently assert that it is necessary to salt out soaps in the presence of an excess of alkali if appreciable hydrolysis is to be avoided. It now appears, however, most probable that acid soaps, which are undoubtedly often observed in large-scale experiments, arise from incomplete saponification. It will be shown in another communication from this laboratory that the final stages of saponification with alkali are surprisingly slow, but that if sufficient time is allowed it is completed to within 99·8 per cent. even when no excess of alkali is present.

The measurements here given show that the hydrolysis of soap curd is slightly greater than that of the same soap in solution (McBain and Martin, T., 1914, **105**, 957; McBain and Bolam, *ibid.*, 1918, **113**, 825). However, the soap fibres are, within a few tenths of a per cent., neutral soap together with water of hydration. Even when salted out by 2·0*N*-sodium hydroxide, the curd fibres are neutral to within 0·5 per cent.

(*b*) *Hydration Values in Presence of Saturated Sodium Chloride.*

In Table I there are three final results with a mean value of 2·1 mols. of H_2O to 1 mol. of NaP. This is from its nature necessarily a minimum value for the hydration, since it is based on the assumption that no sodium sulphate is sorbed by the curd fibres in these circumstances. Occurrence of sorption would lessen the increase in the concentration of the sodium sulphate in the mother-liquor. The value 2·1 mols. of H_2O is probably not greatly in error, as will be seen in Part II.

(*c*) *The Sorption of Sodium Chloride by Curd Fibres.*

In Table I there are three values for the hydration of curd fibres salted out by saturated solution of sodium chloride deduced from the sodium chloride itself, that is, if we ignore the sorption of sodium chloride. These are 0·2, 0·6, and 1·0 instead of 2·0 mols. of H_2O to 1 mol. of NaP. From this deficiency we can deduce the amount of salt sorbed by the sodium palmitate. It is approximately 8·9 grams of NaCl to 1 mol. (278 grams) of NaP; that is, 3·2 per cent. of the weight of the anhydrous sodium palmitate or 2·7 per cent. of the total weight of the curd fibres apart from enmeshed mother-liquor.

In the presence of 2·0*N*-alkali, 2 per cent. sodium chloride indicated a hydration value of 1·5 and 1·9, whereas it was previously shown (*loc. cit*) that the hydration is about 4·0 and 4·6 mols. of H_2O to 1 mol. of NaP. The deficiency here indicates that 1·8 and 0·10 grams of sodium chloride are sorbed by 1 mol. of NaP from 4 and 2 per cent. solutions of sodium chloride respectively in the presence of 2·0*N*-sodium hydroxide or 0·5 and 0·3 per cent. of the total weight of the curd fibres themselves.

Commercial soap contains about 30 per cent. of water. The wet curds of sodium palmitate were more than half water, but of course it would have been easy so to press and drain out just sufficient enmeshed brine to bring the total water contained in them down to 30 grams per 100 grams of curd. Had this been done with the three curds mentioned in the foregoing paragraphs, their empirical composition would have been represented by the formulæ $NaP + 6\cdot6H_2O + 0\cdot59NaCl$; $NaP + 6\cdot6H_2O + 0\cdot063NaCl + 0\cdot094NaOH$; $NaP + 6\cdot6H_2O + 0\cdot029NaCl + 0\cdot07NaOH$. On the other hand, the curd fibres proper contained in these curds have the composition $NaP + 2\cdot1H_2O + 0\cdot15NaCl$; $NaP + 4H_2O + 0\cdot031NaCl$, and $NaP + 4\cdot6H_2O + 0\cdot017NaCl$.

It will be seen that the proportion of sodium chloride which is free in solution in the enmeshed brine is approximately $\frac{3}{4}$, $\frac{1}{2}$, and $\frac{3}{7}$ respectively, the remainder being bound in the curd fibres themselves which are in equilibrium with these brines, lyes, or mother-liquors. It is evident that, by washing, the greater part of the sodium chloride can be removed from the curd as well as from the curd fibres, although in accordance with the behaviour characteristic of sorption the last traces of salt in the curd fibres could never be extracted. Such washing would have to be done by "pickling," a wholly different operation from the washing "changes" involved in the soap-boiling processes which will be discussed in another communication (compare 4th Report on Colloid Chemistry, 1921).

(*d*) *Unsaturated Brine and Adsorption of Sodium Sulphate.*

From a consideration of the results in Table III, and, to a minor extent, experiments 13 and 15, it appears probable that sodium sulphate, like sodium chloride, can be sorbed by curd fibres unless this is prevented by the presence of a great excess of some other electrolyte. It is probable that in the experiments recorded in Table III, where the salting out is effected by much less concentrated sodium chloride, the true hydration of the curd fibres is at least 4·5 mols. of water to 1 mol. of sodium palmitate, whereas the results from the analysis of sodium sulphate give a value 3·3 and those from sodium chloride indicate 3·1. It has already been shown that the sodium chloride is sorbed to a slight extent; here, evidently, the sodium sulphate is sorbed nearly as much, thereby interfering with the full development of the sorption of the sodium chloride. Even sodium hydroxide is affected by sorption, as will be shown in Part III, although to a very minor extent; evidently no ordinary salt is quite satisfactory as reference substance.

The only available data for the various commercial fats and oils are those of Merklen. Using his analytical data for sodium chloride and hydroxide, we deduce hydration values lying between 3·4 and 5·0 mols. of water to 1 mol. of soap in the presence of graining lye (Lessive de cuisson, Siedelauge).

Summary.

1. When sodium palmitate is salted out with nearly saturated solutions of sodium chloride containing a small amount of sodium sulphate the increase in concentration of the sodium sulphate corresponds with a hydration of the neutral curd fibres NaP,2·1H_2O.

2. Sodium chloride is appreciably sorbed by the curd fibres, although even in this case distinct negative sorption is observed.

3. Sodium sulphate, sodium chloride, and, to a very slight extent, sodium hydroxide are each sorbed by the curd fibres except in the presence of a large excess of a second salt. Thus the empirical composition of curd fibres salted out by a saturated solution of sodium chloride corresponds with the proportions NaP : 2·1H_2O : 0·16NaCl; that is, the fibres themselves contain 78·7 per cent. of anhydrous fatty acid and about 3 per cent. by weight of sodium chloride. From more dilute lyes more water and much less salt is sorbed.

In conclusion, we have pleasure in thanking the Colston Research Society of the University of Bristol for the grants towards the purchase of materials and apparatus.

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CLVIII.—*The Hydration of the Fibres of Soap Curd. Part II. The Dew-point Method.*

By JAMES WILLIAM McBAIN and CYRIL SEBASTIAN SALMON.

IN previous communications (T., 1919, **115**, 1300; this vol., p. 1369) it has been shown that the fibres of soap curd are hydrated and that their hydration depends on the concentration of the solution from which they have been salted out. As it was thought desirable to establish the results by some independent procedure, the composition of soap curds was investigated by the dew-point method already described (McBain and Salmon, *Proc. Roy. Soc.* 1920, **97**, [*A*], 44; *J. Amer. Chem. Soc.*, 1920, **42**, 426).

It is clear from the phase rule that in the system—soap curd and saturated brine—evaporation at constant temperature does not lead to any change in vapour pressure until the saturated solution disappears. After this point, the vapour pressure diminishes rapidly, and in the curve obtained by plotting vapour pressure against the total water present a break will be found where the water present is that contained in the soap fibres themselves. The method based on this principle can be applied at various temperatures to curds prepared from different fatty acids and with saturated solutions of one or more salts.

EXPERIMENTAL.

The method used for the measurement of vapour pressure was a variation of the dew-point method used for the measurement of pure soap solutions. Dehydration was carried out by draining off water by means of a strong filter-pump through calcium chloride tubes, and the loss of water was estimated either by weighing these tubes, or by weighing the tube in which the vapour-pressure measurements were carried out, in the same manner as for the measurement of concentrated soap solutions (McBain and Salmon, *loc. cit.*).

The curds were prepared in the following manner: a quantity of palmitic acid was weighed into a silver tube and the alkali and water required for a normal solution were added. Sufficient sodium chloride was then added to ensure that the solution should be fully saturated and the tube sealed with silver wire and plate and shaken for at least a week at 90°. At the end of this time the tube was opened and the contents filtered while still hot through silver gauze. The filtrate was tested for alkalinity to secure that the reaction had become complete. A weighed portion of the curd was then introduced into the tube used for the vapour-pressure measurements and the dehydration carried out as described above.

As soon as the dehydration had proceeded far enough the curd was analysed. The sodium palmitate was estimated by decomposing the soap with a known quantity of hydrochloric acid and titrating the excess with standard alkali and also by titrating in alcohol the palmitic acid liberated. Sodium chloride was estimated by weighing as silver chloride, allowance being made for the hydrochloric acid which had been added.

Hydration Results.

(*a*) *Palmitate Salted out at* 90° *by Saturated Sodium Chloride.*

In Table I the first column for each experiment gives the composition of the curd expressed as mols. of water to 1 mol. of NaP, the second the dew-point lowering as compared with water.

TABLE I.

Expt. I.		Expt. II.		Expt. III.	
Mols. H_2O; 1NaP.	Dew-point lowering.	Mols. H_2O; 1NaP.	Dew-point lowering.	Mols. H_2O; 1NaP.	Dew-point lowering.
16·9	6·69°	18·4	6·54°	19·5	6·49°
16·1	6·70	14·1	6·54	13·4	6·49
10·6	6·70	13·2	6·54	7·35	6·50
10·0	6·70	11·4	6·55	3·31	6·49
5·11	6·71	10·2	6·54	2·11	6·49
4·31	6·71	9·08	6·56	2·09	6·53
2·56	6·71	8·81	6·54	1·09	7·02
2·47	6·72	3·18	6·53		
2·13	7·67	2·21	6·58		
1·99	17·54	2·14	7·49		
1·92	23·40	1·25	8·09		

The dew-point lowering obtained before dehydration is 6·70° (that of a saturated solution of sodium chloride, measured by the dew-point method, was 6·47). This value remains constant until the curd has the composition 1NaP : 2·13H_2O and then increases rapidly.

On comparing the results for different specimens of curds, it will be seen that the horizontal portion of the graph is nearly the same in each case. The slight difference is probably due to the capillary attraction of the solid soap for the mother-liquor. The break in each case occurs at a composition between 1NaP : 2·09H_2O and 1NaP : 2·21H_2O.

Table II gives the complete details of the composition of the curd at the break.

TABLE II.

Composition of the Curd at the Break in the Vapour Pressure Curve.

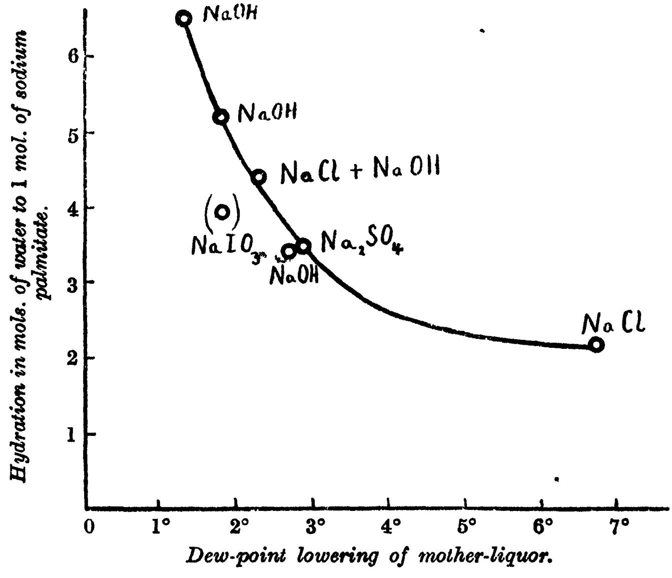
Total weight of curd. Grams.	Grams of NaP.	Grams of NaCl.	Grams of H_2O (by difference).	Mol. H_2O to 1NaP.
3·571	2·112	1·167	0·292	2·13
4·880	1·773	2·853	0·254	2·21
5·441	2·632	2·453	0·356	2·09

From these results the composition of the sorption compound or hydrated fibres is 1NaP : 2·14H_2O, giving the total amount of sorbed water.

The question might be raised as to whether the values obtained for curds prepared in this manner would be the same for curds salted out from true neutral solutions, since it is evident that these solutions can never actually become neutral. In short, what is the effect of the method of preparation on the composition of the curd? To decide this point an experiment was carried out in the following manner. A weighed quantity of a 1·0*N*-solution of sodium palmitate was introduced into the vapour-pressure tube and then slightly more salt added than was necessary for saturation. The mixture was then well shaken and after it had remained at 90° for some hours dehydration was carried out as before. This method of preparation gave us the composition of the sorption compound 1NaP : 2·24H_2O. This is the same, within the experimental error, as that given by the previous method.

Fig. 1.

Relation between hydration and vapour pressure of soap fibres studied by different methods.



The composition of the solid portion of the curd, then, is independent of the way in which it is prepared.

Since in the latter case the curd is salted out from a solution of varying composition (although the total amount of water present is the same), the solid constituent of the curd must be in true equilibrium with the water present. This equilibrium was apparently reached in about one hour.

(*b*) *Palmitate Salted out at Lower Temperatures.*

The composition of these curd fibres was investigated at 50° and at 16°. The curds were all prepared at 90°, but were kept at the lower temperature for some time before examination. The compositions of the curds are given in Table III, including those obtained for 90° in Tables V and VII.

TABLE III.

Composition of the Curd Fibres at Various Temperatures.

Temperature.	Grams of NaP.	Grams of NaCl.	Grams of H_2O.	Mols. H_2O to 1NaP.
90°	—	—	—	2·16
80	1·802	2·734	0·271	2·32
	1·288	1·800	0·200	2·40
16	1·505	2·186	0·254	2·60

At lower temperatures more water is sorbed and this change in composition of the sorption compound with decreasing temperature, although small, appears to be fairly regular.

(*c*) *Palmitate Salted out with Sulphate or Iodate at* 90°.

Unfortunately, in the experiments with sodium iodate in Table IV the amount of water was estimated by difference and it is therefore open to some uncertainty, since the iodate may have been partly decomposed before analysis.

TABLE IV.

Hydration of Palmitate Fibres Salted out by Saturated Sodium Sulphate or by Saturated Sodium Iodate.

	By Na_2SO_4.		By $NaIO_3$.	
	I.	II.	I.	II.
Weight of NaP	1·627	1·824	2·041	1·248
„ „ Na_2SO_4 or $NaIO_3$	1·904	2·516	1·864	1·187
„ „ H_2O	0·372	0·923	0·523	0·316
Mols. H_2O : 1NaP	3·52	3·58	3·96	3·89

(*d*) *Laurate Salted out at* 90° *with Saturated Sodium Chloride.*

A normal solution of sodium laurate was prepared by the first method and gave the following composition for the curd at the break in the vapour-pressure curve.

Weight of NaL = 1·268 grams
„ „ NaCl = 1·453 „
„ „ water = 0·185 „

Composition of sorption compound, 1NaL : $1·80H_2O$.

There is less sorption with sodium laurate than with sodium palmitate. This was to be expected, for it would seem probable that less water would be taken up as the fatty acid series is descended.

Sorption of Sodium Chloride by Palmitate Fibres at 90°.

In Part I it was found that during salting out the increase in concentration of sodium chloride is distinctly less than that of the sodium sulphate also present. This was explained as being due to sorption of sodium chloride by the curd fibres, the sorption being greatest in the presence of a solution of sodium chloride and there amounting to 3 per cent. by weight of the anhydrous sodium palmitate.

This conclusion has been checked by a modification of the dew-point method in which solutions were used which were not quite saturated with sodium chloride and the dehydration was carried out as before. The results obtained for two specimens of curd are shown in Table V.

TABLE V.

Dehydration at 90° of Wet Curds from nearly Saturated Brine.

I.		II.	
Mols. H_2O ; 1NaP.	Dew-point lowering.	Mols. H_2O ; 1NaP	Dew-point lowering.
27·4	6·42°	26·0	6·44°
22·9	6·46	23·3	6·47
21·5	6·48	22·6	6·47
19·0	6·49	17·0	6·47
2·28	6·49	7·57	6·48
2·21	6·49	2·11	6·47
2·09	6·53	2·08	6·50
1·86	6·66	2·04	6·58
1·76	9·99		

At first the dew-point lowering is 6·42° (that is, less than that of a saturated solution of sodium chloride), it then increases to 6·49° (the figure for a fully saturated solution) and remains constant for some time, but finally commences to rise rapidly. The point at which this rise occurs corresponds with the break observed previously and occurs at a composition 1NaP : $2{\cdot}08H_2O$, the same as for curds salted out by fully saturated sodium chloride.

The horizontal portion of the curve corresponds with the amount of water just necessary to dissolve the sodium chloride present in the mother-liquor. The total amount of sodium chloride present in the wet curd is estimated directly by analysis. The difference between these two values gives the amount of sodium chloride sorbed. This can also be calculated in the way indicated in Part I. The mother-liquor separated by filtration was analysed for sodium chloride and a value obtained for the water sorbed calculated from the increase in concentration. From the difference between the value obtained in this way and that given by the vapour-pressure method, the amount of salt absorbed can be calculated.

Table VI contains the results of these analyses.

The first column gives the weight of sodium palmitate in the curd, the second the composition given by the vapour-pressure curve, the third the composition calculated from the increase in concentration of the mother-liquor, the fourth the weight of sodium chloride calculated from the horizontal portion of the curve, and the last the weight of sodium chloride directly estimated by analysis.

TABLE VI.

	Mols. H_2O : 1NaP.		NaCl (grams).	
NaP (grams).	From vapour-pressure curve.	From increase in conc. of mother-liquor.	From graph.	By analysis.
2·568	2·08	1·4	1·39	1·47
1·02	2·11	1·4	0·49	0·50

The amounts of sodium chloride sorbed are :

Expt. I. Calculated from columns 2 and 3 = 1 per cent. of the weight of NaP.
" " " 4 and 5 = 3 " " " "
Expt. II. " " " 4 and 5 = 1 " " " "

The agreement between these results is not very good, but each method shows that curd fibres sorb sodium chloride to the extent of between 1 and 3 per cent. by weight of the sodium palmitate contained in them, that is, in the presence of saturated sodium chloride. This may be compared with the 0·5 and 0·3 per cent. by weight observed in Part I for the sorption in the presence of 2·0*N*-sodium hydroxide containing only 4 per cent. and 2 per cent. respectively of sodium chloride.

Discussion.

The whole of this work affords strong evidence for the conception of the nature of soap curds advanced in previous communications from this laboratory (for reference, see Part I). In the instances here discussed, where concentrated solutions of electrolytes are concerned, the solubility of the curd fibres is excessively small. On the other hand, in pure water at higher temperatures they are extremely soluble and the so-called melting point of aqueous soap curds is the temperature at which the whole of the fibres have just passed into solution * and the hard, opaque curd has finally turned to transparent liquid or gel.

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* This interpretation is borne out by the following determinations of the lowering of dew-point of soap solutions in the neighbourhood of their melting

The agreement between the hydration values obtained by measurements of dew-point and those by the methods of sorption and indirect analysis (T., 1919, **115**, 1300; this vol., p. 1369) is quite satisfactory. For curds of sodium palmitate salted out by saturated or nearly saturated solutions of sodium chloride at 90°, we here obtain as the mean of six closely agreeing experiments 2·16 mols. of H_2O to 1 mol. of NaP, whereas in Part I the result was 2·1 mols. of H_2O to 1 mol. of NaP.

The dew-point method gives maximum values, whereas the methods of sorption and indirect analysis give minimum values, so that it is evident that the degree of hydration has been determined for this case within very narrow limits even when it is recalled that the results in Part I are to some extent affected by the influence of a lower temperature.

A comparison of the degrees of hydration obtained for sodium palmitate at 90° in the presence of various concentrations of the different salting-out media indicates that the chief factor concerned is the concentration and that possibly the hydration of the fibres may depend solely upon the vapour pressures of their mother-liquors. This result would be in accordance with the studies of conductivity recorded by Laing and McBain (*loc. cit.*), and is borne out by the results of previous measurements (*loc. cit.*) collected in Table VII.

TABLE VII.

Hydration of NaP *at 90° compared with the Vapour Pressure of the various Mother-liquors.*

Salt.	Concentration.	Dew-point lowering.	Hydration.
NaCl	6·1*N* *	6·47°	NaP : 2·1H_2O
Na_2SO_4	2·6*N* *	2·89	3·5
NaOH	3·0*N*	2·7	3·4
NaCl+NaOH	2·0 + 0·5*N*	2·3	4·4
$NaIO_3$ †	1·75*N*	1·81	(3·9)
NaOH	1·9*N*	1·8	5·2
NaOH	1·5*N*	1·3	6·5

* Saturated solution. † Analysis open to some uncertainty.

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and solidification temperatures. It is seen that there is no sudden disappearance of such lowering when solidification sets in, thus showing that the greater portion of the soap is still in solution.

Soap.	Temperature.	State.	Dew-point lowering.
1·0*N*-NaP	70°	glassy viscous liquid	0·26°
	67	opaque solid	0·26
1·5*N*-NaL	43	liquid	0·30
	40	liquid (supercooled)	0·30
	40	solid	0·28
0·5*N*-KP.	33	turbid liquid	0·17
	27	solid	0·16

If this hypothesis is confirmed, it introduces an important simplification into the consideration of these systems, and in any case it is shown to be true as a close approximation. It is quite reasonable that the hydration of soap fibres should be a function of the aqueous vapour pressure if they are not much contaminated with salt. From this it should be possible to calculate the hydration of fibres crystallising out from pure aqueous solution where no salts are present. An attempt is now being made to test this by experiment.

It should ultimately be possible to determine the real hydration of a commercial soap simply from a knowledge of its vapour pressure at room temperature or from an analysis of any drops of "sweat" exuding from it.

It is interesting to note that the relationship between vapour pressure and degree of hydration is the exact opposite of that so characteristic of adsorption. Adsorption is most prominent at low pressures, and is but little affected by subsequent great increase of pressure, whereas here small increase in the already high vapour pressure increases the amount of hydrate water several-fold.

The form of the curve resembles that which would be obtained for one of three possibilities; the progressive filling of pores, or the gradual dilution of a solution, or the formation of a chemical compound in solid solution in which the dissolved molecule would contain 5 or 10 molecules of water. Investigation should yield most interesting results, for there are special difficulties in the way of each of these interpretations. The phenomenon is certainly not merely one of the filling of pores, for this would not lead to the apparent negative sorption, and would not account for the agreement between the results of Parts I and II of this series and, moreover, the points in Fig. 1 refer to quite different specimens of curd. The second suggestion would require the curd fibres to behave as aqueous solutions of soap. According to the third suggestion, anhydrous NaP would have to be the solvent with either at least pentamolecular water in a pentahydrate of a polymerised NaP as dissolved substance; but the curvature varies between that required for 5 and for 10 molecules of water. It is evident that the facts do not agree with any of our ordinary conceptions and perhaps a more purely chemical explanation is required. For instance, colloidal particles may be postulated which possess a large number of free secondary valencies of graduated strength, of which the weakest are the most numerous.

The dehydration curve for curd fibres which we are here discussing corresponds with the portion O_0O_1 of von Bemmelen's classical dehydration curves for such gels as those for silica after they have completed the intermediate opaque stage and have become clear again. Von Bemmelen found in some cases the same form of curve, although the curvature is not nearly so pronounced, and he showed that the hydration and dehydration curves coincided, so that the process was reversible.

Summary.

(1) A device for the study of the hydration of colloids and for the measurement of the amounts of salt sorbed by them is the study of their vapour pressures during gradual dehydration in the presence of saturated or nearly saturated solutions of one or more salts.

(2) In the case of soap curds the results of the dew-point method are in close agreement with those obtained by the methods of negative sorption and indirect analysis.

(3) The degree of hydration of the fibres of soap curd depends almost entirely on the vapour pressure of the solution with which it has been in contact, being least for the most concentrated brines.

(4) There is a small but real increase in hydration with lowering of temperature.

(5) The hydration of sodium palmitate is distinctly greater than that of either the laurate or stearate.

(6) The slight sorption of sodium chloride by curd fibres is confirmed, thus affording an instance of real positive sorption in a case of apparent negative sorption.

In conclusion, we desire to express our thanks to the Colston Research Society of the University of Bristol and to the Research Fund Committee of the Chemical Society for generous grants.

THE CHEMICAL DEPARTMENT,
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CLIX.—*Ethyl Hydrogen Sulphate.*

By HORACE BARRATT DUNNICLIFF and GERALD SNOWDEN BUTLER.

HENNEL (*Trans. Roy. Soc.*, 1826, 240; 1828, ii, 365), using equal parts of alcohol of specific gravity 0·82 and oil of vitriol, obtained 56 per cent. conversion of the sulphuric acid present into ethyl hydrogen sulphate. Berthelot (*Bull. Soc. chim.*, 1873, [ii], **19**, 227) showed that the reaction takes some time to complete. He worked at the temperature of the water-bath and, with molecular quantities of alcohol (94 per cent.) and sulphuric acid, obtained a maximum esterification of 59 per cent. of the sulphuric acid after twenty days. He also showed that, with 79 per cent. alcohol and oil of vitriol, the maximum esterification was 54·8 per cent. after one hundred and forty-seven days. Claesson (*J. pr. Chem.*, 1879, [ii], **19**, 246) found that, when absolute alcohol is used, a maximum esterification of 77·4 per cent. of the sulphuric acid is obtained. He showed that the relation $\frac{\text{actual esterification obtained}}{\text{maximum esterification possible}}$ is a minimum (0·571) when the two reacting substances are present in molecular proportions. In the present paper, these points and also the statics and dynamics of the esterification are investigated.

Preparation and Estimation of Alcoholic Sulphuric Acids.

Alcoholic sulphuric acids were made by adding 100 per cent. ethyl alcohol in small quantities at a time to cooled 100 per cent. sulphuric acid (T., 1920, **117**, 651). It was not found possible to make an alcoholic sulphuric acid of an exact strength by mixing weighed quantities of the two constituents, but the concentration always approximates to the desired proportions. For example: in a particular case, the approximate strengths of a series of alcoholic sulphuric acids estimated by weighing were 20, 25, 30, 35, and 40 per cent. of sulphuric acid. The actual strengths, as determined by titration, were 20·41, 25·04, 30·13, 35·59, and 40·42 per cent. respectively. Many unsuccessful attempts were made to obtain a mixture in exact molecular proportions (68·06 per cent. of H_2SO_4).

The following methods for the estimation of ethyl hydrogen sulphate in alcoholic sulphuric acids were examined.

(1) A weighed quantity of the ester was diluted with water. The acidity due to free sulphuric acid and the ester was neutralised

by the addition of pure barium carbonate. Insoluble barium sulphate and soluble barium ethyl sulphate were formed. The barium sulphate and carbonate were filtered off and washed. The filtrate and washings were acidified with dilute nitric acid, barium nitrate was added, and the whole evaporated to pastiness. The residue was taken up with dilute nitric acid and the precipitate of barium sulphate filtered off, washed, dried, and weighed. From the weight of barium sulphate obtained, the amount of ethyl hydrogen sulphate ($BaSO_4 \times 0{\cdot}5403$) was found and its percentage calculated. This method was shown to be tedious and inaccurate, mainly on account of the difficulties of filtration and washing, and the resultant bulk of filtrate to be handled.

(2) A weighed quantity of alcoholic sulphuric acid was diluted with water and an excess of barium hydroxide solution added. The barium sulphate was filtered off and the filtrate and washings were evaporated with dilute nitric acid to pastiness. The residue was extracted with dilute nitric acid and the procedure completed as described above (1). This method is less troublesome than the former, but it is slow, and consistent results were not easily obtained.

(3) (α) A weighed quantity of alcoholic sulphuric acid was titrated against standard sodium or potassium hydroxide. The percentage of free acid, b, was calculated as sulphuric acid.

(β) A further volume of standard alkali, equal to that used in the previous titration, was then run into the basin. The solution was evaporated as nearly to dryness as possible on a water bath and then heated in an air-oven for half an hour at 120°. This ensures complete decomposition of the ethyl hydrogen sulphate. The solid residue was taken up with distilled water and the excess of alkali estimated by standard acid. From the total quantity of alkali neutralised by the alcoholic sulphuric acid in both stages α and β, the percentage of sulphuric acid, a, in the mixture before any esterification took place was calculated. Hence, the percentage of ethyl hydrogen sulphate in the alcoholic sulphuric acid is $2(a-b) \times 126/98$ and the percentage esterification of the sulphuric acid present is $2(a-b) \times 100/a$. The accuracy of this method has been established by a number of analyses.

(4) A weighed quantity of alcoholic sulphuric acid was titrated against standard alkali and the percentage acidity, x, calculated as sulphuric acid. The sulphuric acid which had not been acted on by alcohol was estimated directly, in a fresh portion, by precipitation with barium chloride or nitrate.

If in W grams of alcoholic sulphuric acid taken, the free sulphuric acid found is W_1 grams (wt. of $BaSO_4 \times 0{\cdot}42023$), then the percentage of free sulphuric acid present is $100W_1/W$. Therefore the percentage of ethyl hydrogen sulphate in the alcoholic sulphuric acid is $2(x-100W_1/W)\times 126/98$. A comparison between results obtained by methods 3 and 4 showed close agreement.

(5) The estimation of mixtures of alcohol, sulphuric acid, and water is dealt with by the authors in *J. Soc. Chem. Ind.*, 1920, **39**, 146T. The method described is applicable to the analysis of the alcoholic sulphuric acids dealt with in this paper. In practice, however, the approximate strength was obtained by weighing and the actual strength determined by titration (method 3 above).

An attempt was made to prepare pure ethyl hydrogen sulphate from alcoholic sulphuric acids by (1) extraction of alcohol from the mixture by light petroleum and (2) the subsequent extraction of sulphuric acid and water from the residue of ester, sulphuric acid, and water by means of dry ether. An apparatus of the Soxhlet type was specially designed for the extraction of a liquid by a liquid. In both cases the mixture increased in bulk when acted on by the solvent and the method was unsuccessful. From the work done so far, it appears that ethyl hydrogen sulphate is slightly soluble in ether. This observation is contrary to statements in most works of reference, and requires further investigation.

Application of the Law of Mass Action.

In order to determine whether this esterification follows the law of mass action, thirty mixtures were made up and allowed to come to equilibrium at the temperature of the laboratory (about 18—19°). The equilibrium point is not sensitive to small changes of temperature.

Let a reaction mixture be made of m gram-molecules of ethyl alcohol, n gram-molecules of sulphuric acid, and y gram-molecules of ethyl hydrogen sulphate (or water). Then, in the condition of equilibrium, if x denotes the number of gram-molecules of ethyl hydrogen sulphate (or water) formed as a result of the interaction of the above quantities of alcohol and sulphuric acid, there exists the relation :

$$\frac{(m-x)(n-x)}{x(x+y)} = \text{a constant quantity} = K \quad . \quad . \quad . \quad . \quad (1)$$

(The volume of the reaction mixture is unchanged.)

But all the mixtures were made up with 100 per cent. sulphuric acid and 100 per cent. alcohol. Hence $y=0$. Therefore, by always making $n=1$, the relation becomes

$$\frac{(m-x)(1-x)}{x^2} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The results of a typical series of experiments are given in Table I.

TABLE I.

	Gram-mols. of alcohol per gram-mol. of sulphuric acid.	Gram-mols. of ethyl hydrogen sulphate. Observed.	Calculated, using $K = 0·620$ in $\frac{(m - x)(1 - x)}{x^2} = K$.	Constant obs. $\frac{(m - x)(1 - x)}{x^2} = K$.	
	m	x (obs.).	x (calc.).	K	
1	8·353	0·8650	0·9301	1·3510	
2	6·306	0·8461	0·9040	1·1730	
3	4·930	0·8555	0·8800	0·8042	
4	3·950	0·8480	0·8520	0·6557	
5	3·089	0·8101	0·8197	0·6594	
6	2·0965	0·7330	0·7448	0·6776	
7	1·3846	0·6441	0·6467	0·6349	*
8	1·0000	—	0·5595	0·6200	
9	0·9128	0·5450 (0·5970)	0·5380 (0·5894)	0·5635	
10	0·5730	0·4100 (0·7155)	0·4026 (0·7025)	0·5722	
11	0·5320	0·3888 (0·7308)	0·3851 (0·7240)	0·5789	
12	0·2210	0·2051 (0·9283)	0·1927 (0·8720)	0·3004	

* The value for K is the mean of Nos. 4—11. There appears to be considerable disparity between the values for K, of which an average is taken, but the value found for K is very sensitive to small differences in the observed values in column 3. The variation, dK, in K for a small change in x, such as might be caused by experimental error, is found as follows :

$$\frac{dK}{dx} = \frac{d}{dx}\left(\frac{(m - x)(1 - x)}{x^2}\right) = -\frac{2m}{x^3} + \frac{m + 1}{x^2}$$

$$dK = \left(\frac{(m + 1)}{x^2} - \frac{2m}{x^3}\right) dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

By substitution in this expression, it is found that, for the various values of m investigated, the variation in the value of K is not less than five times the variation in the value of x (Table I, Nos. 4—11). The law is thus shown to hold when the molecular proportions of alcohol to sulphuric acid vary between 4 : 1 (80 per cent. sulphuric acid) and 0·5 : 1 (35 per cent. sulphuric acid). Below 20 per cent. sulphuric acid, the values for K rapidly increase, the constant for 4·5 per cent. sulphuric acid being 11·0.

The values shown in brackets in columns 3 and 4 give the fraction of a molecule of ester found and calculated (assuming $K = 0·62$) respectively from one molecule of alcohol in alcoholic sulphuric acids of the concentrations shown in column 2. Thus, the numbers in brackets in columns 3 and 4, together with those in the same columns above them, give respectively, for the concentrations shown in column 2, the observed and calculated values for the relationship,

$$\frac{\text{actual esterification obtained}}{\text{maximum possible esterification}},$$

the denominator of the fraction being unity in each case. The value 0·5595, calculated for molecular quantities of the reacting substances on the basis of the constant experimentally obtained, is comparable with that (0·571) obtained by Claesson (*loc. cit.*). His observation that the above ratio is a minimum when molecular quantities of the reacting substances are employed is also confirmed. He obtained a maximum esterification of 77·4 per cent. of the sulphuric acid. From Table I it will be seen that esterifications of sulphuric acid up to 86·5 per cent. (No. 1) and of alcohol up to 92·8 per cent. (No. 12) have been obtained. A large excess of sulphuric acid does not cause quantitative esterification of the alcohol. When a large excess of alcohol (more than 80 per cent.) is present, the value of the above relationship gradually diminishes. This result can be seen from the figure in T., 1920, **117**, 656.

The law of mass action fails at high concentrations of either component of the reaction mixture.

The Velocity of the Reaction.

Previous observations (*loc. cit.*) that, at the ordinary temperature, the mixtures take a considerable time to attain equilibrium have been confirmed. The reaction is never complete at once, even when the two substances are mixed rapidly, and the rise in temperature amounts to 20°. When carefully mixed, a decrease in acidity is observed for fourteen to twenty days, depending on the strength of the alcoholic sulphuric acid under examination. Attempts were made to determine the order and velocity of the reaction in mixtures of low sulphuric acid concentration. Alcohol was added to sulphuric acid with stirring and external cooling, but considerable local heating occurred and the initial stages of the reaction proceeded irregularly, but with very considerable velocity. The strengths of the several mixtures investigated lay between 13·18 and 4·50 per cent. of sulphuric acid, and thus never contained less than 14 molecules of alcohol to one of sulphuric acid.

Considerable difficulty was experienced in maintaining the mixtures at the comparatively low temperatures employed over intervals of from several days to a fortnight. The percentage of ester was estimated daily until it was constant. In the example given in Table II, this took sixteen days. In the condition of equilibrium, 12·6 is the maximum possible percentage of ester in an alcoholic sulphuric acid of this concentration (11·12 per cent. of H_2SO_4). The first estimation of ethyl hydrogen sulphate after mixing the constituents, showed the presence of 8·38 per cent. of ester. In this case, therefore, the reaction was about two-thirds completed immediately after mixing. Let a=the molecular concentration of sulphuric acid, b = the molecular concentration of alcohol at the time of mixing, and x = the molecular concentration of the ester on the mixture after time t. Then, if the reaction is of the first order,

$$\frac{1}{t}\log_e\frac{a}{a-x} = \text{a constant } (K) \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

and if it is of the second order,

$$\frac{1}{t}\log_e\frac{a(b-x)}{b(a-x)} = \text{a constant } (\mathrm{K}_1) \quad . \quad . \quad . \quad . \qquad (5)$$

Using the successive values for x shown in Table 2, K and K_1 become :

K — 0·4389, 0·2399, 0·1931, 0·1543, 0·1280, 0·1134, and
K_1 = 0·4225, 0·2312, 0·1867, 0·1493, 0·1239, 0·1099.

Examination of these results shows that allowance must be made for the ester initially present. It further invites attention to the relatively small value of the factor $(b - x)/b$ and suggests that, at small concentrations of sulphuric acid at any rate, the reaction is of the first order.

If, in order to eliminate the disturbed period, the velocity of the reaction is determined from the time at which the first estimation is made, the ester initially present must be allowed for by deducting, both from the molecular concentration of the sulphuric acid and from the molecular concentration of the ester present at each successive determination (Table II, col. 1), an amount equal to the initial concentration of the ester (0·0665). Thus, from Table II, the corrected concentration of the sulphuric acid will be (0·1135 — 0·0665) or 0·0470 gram-molecule and the corrected amount of ester produced after the first interval of time will be (0·0722 — 0·0665) or 0·0057 gram-molecule—and so on.

In this case, the values for K are

0·0561, 0·0485, 0·0655, 0·0586, 0·0514, 0·0496

and those obtained for K_1 are no more consistent.

An attempt was therefore made to determine how many days' reaction at normal velocity is represented by the initial concentration of 0·0665 gram-molecule of ester.

This was calculated from the equation

$$\frac{1}{z}\log_e\left(\frac{a}{a-x_1}\right)=\frac{1}{z+t}\log_e\left(\frac{a}{a-x}\right)\quad .\ \ .\ \ .\ \ .\quad (6)$$

in which z is the number of days which must be added to the observed time t, a is the molecular concentration of sulphuric acid, x is the molecular concentration of the ester after the observed time t, and x_1 is the initial molecular concentration of the ester.

Since $a = 0{\cdot}1135$ and $x_1 = 0{\cdot}0665$, equation (6) becomes

$$\frac{1}{z}\log_e\left(\frac{0{\cdot}1135}{(0{\cdot}1135-0{\cdot}0665)}\right)=\frac{1}{z+t}\log_e\left(\frac{0{\cdot}1135}{(0{\cdot}1135-x)}\right)$$

or

$$z=\frac{0{\cdot}3829t}{0{\cdot}6721-\log_e(11{\cdot}35-100x)}\quad .\ \ .\ \ .\ \ .\ \ .\ \ .\quad (7)$$

Substituting in (7) for x and t (Table II, cols. 1 and 2)

$$z = 6{\cdot}8 \text{ days (average).}$$

When 6·8 days are added to the observed times of the reaction, the values for K calculated for a unimolecular reaction become constant within the experimental error (Table II, col. 4). The values for K_1, the constant as calculated by equation (5) for a bimolecular reaction, are successively:

0·0541, 0·0517, 0·0526, 0·0572, 0·0553, 0·0525, 0·0515.

The reaction is, therefore, of the first order.

TABLE II.

Sulphuric acid = 11·12 per cent. = 0·1135 gram-molecule.
Alcohol = 88·88 per cent. = 1·932 gram-molecules.
Temperature of reaction, 18—19°.

Ethyl hydrogen sulphate as gram-mols. per 100 parts by weight of mixture.	Actual time in days.	Actual time + 6·8 days.	$\frac{1}{t_1}\log_e\frac{a}{a-x}$ $a = 0{\cdot}1135$.
x	t	t_1	K
0·0665	0	6·8	0·0563
0·0722	1	7·8	0·0563
0·0759	2	8·8	0·0545
0·0836	3	9·8	0·0591
0·0861	4	10·8	0·0572
0·0875	5	11·8	0·0543
0·0898	6	12·8	0·0532
		Mean	0·0558

These results indicate that, owing to irregularities at the commencement of the reaction, esterification equivalent to 6·8 days' action at 18—19° is accomplished in a few minutes. As soon as the mixing is complete and the system has cooled to 18—19°, the formation of ethyl hydrogen sulphate proceeds normally as a unimolecular reaction. Similar results were obtained with other mixtures, the maximum strength of which corresponded with 13·18 per cent. of sulphuric acid. The order of the reaction at higher concentrations is being investigated. The authors found that ethyl hydrogen sulphate is formed when pure dry alcohol acts upon pure dry sodium hydrogen sulphate (T., 1920, **117**, 652). A rise of temperature of 20° may be observed when the two substances are mixed, but the temperature of this reaction is more easily controlled than that of the action of alcohol upon sulphuric acid. Without the assistance of a cooling agent, a 10 per cent. solution of sulphuric acid in alcohol may be made by the cautious addition of sodium hydrogen sulphate to alcohol—the rise of temperature being 2—3°. When this method of preparation is used, the abnormally high formation of ethyl hydrogen sulphate in the opening stages of the reaction is much smaller than when alcohol and sulphuric acid are mixed directly. The average value found for z, using the expression (8) deduced from equation (6) after substituting 0·01 for a and 0·0084 for x_1, is 0·59 day.

$$z = \frac{0{\cdot}0381\,t}{0{\cdot}9619 - \log_e(10 - 100x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

In Table III are given the values for the constant calculated for a unimolecular reaction, both for the actual times observed and for the actual times plus 0·6 of a day.

TABLE III.

Sulphuric acid = 9·80 per cent. = 0·10 gram-molecule.
Alcohol = 90·20 per cent. = 1·961 gram-molecules.
Temperature of reaction, 18—19°.

Ethyl hydrogen sulphate as gram-mols. per 100 parts by weight of mixture.	Actual time in days.	$\frac{1}{t}\log_e\frac{a}{a-x}$ $a = 0{\cdot}10$.	$\frac{1}{t+0{\cdot}6}\log_e\frac{a}{a-x}$ $a = 0{\cdot}10$.
x	t	—	K
0·0084	0	—	0·0635
0·0214	1	0·1046	0·0654
0·0325	2	0·0853	0·0656
0·0410	3	0·0764	0·0636
0·0498	4	0·0748	0·0651
0·0565	5	0·0723	0·0646
0·0634	6	0·0727	0·0662
0·0657	7	0·0664	0·0612
		Mean	0·0644

Further experiments were carried out in which special precautions were taken to maintain a low temperature while the sodium hydrogen sulphate was being mixed with the alcohol. The bisulphate was added to the alcohol in small quantities at a time with stirring and the reaction vessel was cooled in a freezing mixture. The mixture was then allowed to come to the reaction temperature. In this way a constant for a unimolecular reaction was obtained and no allowance had to be made for a disturbed initial period. The results are given in Table IV.

TABLE IV.

Sulphuric acid = 9·90 per cent. = 0·101 gram-molecule.
Alcohol = 90·10 per cent. = 1·959 gram-molecules.
Temperature of reaction, 15°.

Ethyl hydrogen sulphate as gram-mols. per 100 parts by weight of mixture. x	Actual time in days. t	$\frac{1}{t}\log_e\frac{a}{a-x}$ $a - 0·101.$ K
0·00265	0	—
0·00592	1	0·0262
0·0102	2	0·0231
0·0163	3	0·0255
0·0218	4	0·0264
0·0257	5	0·0255
0·0286	6	0·0241
	Mean	0·0251

This work was done at the Cordite Factory, Aruvankadu, and is published with the permission of The Indian Munitions Board.

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CLX.—*Studies on the Configuration of αα'-Dibromodibasic Acids. Part I. The Dibromoadipic Acids. Synthesis and Resolution of* trans-cyclo*Pentane*-1 : 2 : 3-*tricarboxylic Acid.*

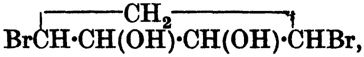
By WILLIAM HENRY PERKIN, jun., and ERIC ROBINSON.

THE bromination of the normal dibasic aliphatic acids leads to the formation of αα'-dibromo-acids, $CO_2H{\cdot}CHBr{\cdot}[CH_2]_n{\cdot}CHBr{\cdot}CO_2H$, which exist in the *meso*- and *racemic* modifications indicated by theory.

Thus succinic acid yields two dibromosuccinic acids, one of which (A) sublimes between 250 and 280° and dissolves in 50 parts of water, whereas the other (B) melts at 167° and is readily soluble in water. These acids are decomposed by boiling with water or dilute alkalis with the formation of both mesotartaric and racemic acids, the former predominating in the case of (A) and the latter in the case of (B), but the relative amounts of these acids produced in the two cases seem to depend on the concentration of the alkali and the time of boiling.

Clearly this decomposition does not afford sufficient evidence on which to base a decision as to the configurations of the two dibromo-acids (A) and (B).

A dibromoglutaric acid, $CO_2H\cdot CHBr\cdot CH_2\cdot CHBr\cdot CO_2H$, melting at 169—170° was first obtained by Auwers and Bernhardi (*Ber.*, 1891, **24**, 2229) from glutaric acid by bromination in the presence of phosphorus. Thiele (*Annalen*, 1900, **314**, 303) subsequently obtained the same acid—which he terms inact.-αγ-dibromoglutaric acid—by the oxidation of *cis*-1 : 4-dibromo-2 : 3-dihydroxy*cyclo*pentane,



$$\overbrace{\mathrm{BrCH\cdot CH(OH)\cdot CH(OH)\cdot CHBr}}^{\mathrm{CH_2}},$$

with permanganate. The isomeric acid—called by Thiele (*loc. cit.*, p. 306) *rac.*-αγ-dibromoglutaric acid, resulted in a similar manner from the oxidation of *trans*-1 : 4-dibromo-2 : 3-dihydroxy*cyclo*pentane and melted at 142—143°. No evidence is brought in proof of the configurations which Thiele assigns to the dibromodihydroxy*cyclo*pentanes and to the dibromoglutaric acids which they yield on oxidation.

The action of bromine on adipic acid has been investigated by Auwers and Bernhardi (*Ber.*, 1891, **24**, 2231), by Rosenlew (*Ber.*, 1901, **37**, 2091), and by Le Sueur (T., 1908, **93**, 718). When two molecular proportions of bromine react with the acid chloride of adipic acid, the two dibromoadipic acids, $CO_2H\cdot CHBr\cdot CH_2\cdot CH_2\cdot CHBr\cdot CO_2H$, required by theory are produced and differ greatly in melting point and particularly in solubility in water. The less fusible acid (C), m. p. 193°, is almost insoluble in cold water, whereas the isomeride (D), m. p. 139°, dissolves very readily.

Rosenlew (*loc. cit.*, p. 2092) converted the two isomerides (C) and (D) into the corresponding dihydroxyadipic acids, $CO_2H\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CO_2H$, by boiling with water and barium hydroxide and states that the acid from (C) melts at 173° and that from (D) at 134°, the latter being the more readily soluble in water.* He concluded from their melting points and relative solubilities that the isomeride of m. p. 173° is the *racemic* and that of m. p. 134° is the *meso*-acid, but brought no evidence in support of this view. Le Sueur (*loc. cit.*) subsequently prepared the dihydroxyadipic acids from the nearly pure dibromo-acid

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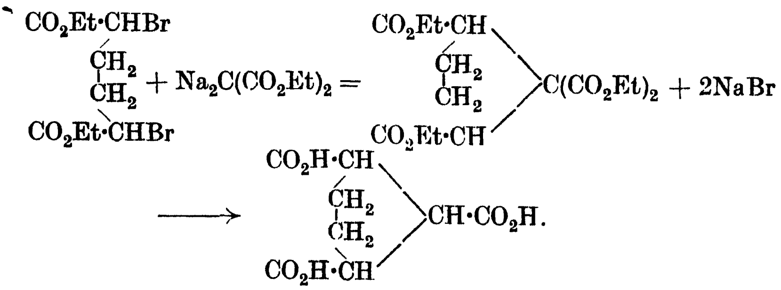
* Rosenlew calls these the dioxyadipic acids A- and B-.

(C) * by boiling with water and sodium hydroxide and showed that two acids (E) and (F) melting at 174° and 146° are produced together and these obviously correspond with the acids melting at 173° and 134° obtained by Rosenlew from the isomeric dibromo-acids in the manner mentioned above.

It appears therefore that the less fusible dibromoadipic acid (C) behaves in a similar manner to the dibromosuccinic acid (A) of high m. p., and yields, on decomposition with water and dilute alkali, a mixture of the *meso-* and *racemic* acids. In order to decide which of the two acids (E) and (F) is the *racemic* and which the *meso-*acid, Le Sueur treated the acid (F) (m. p. 146°) with cinchonidine and obtained a crystalline salt which, on decomposition with ammonia, yielded a *d*-dihydroxyadipic acid of $[\alpha]_D + 3{\cdot}8°$, and he concludes that the acid (F), contrary to the view of Rosenlew, is the *racemic* acid, and that the acid (E) (m. p. 174°) must therefore be the *meso*-acid.

Although there can be little doubt that this view is the correct one, it is clear that the determination of the nature of the dihydroxyadipic acids does not afford valid evidence of the configurations of the dibromo-acids from which they are derived. It seems, indeed, unlikely that decomposition by alkali will lead to a decision in cases of this kind owing to change of configuration which so readily takes place during the replacement of Br by OH. In considering this matter, it occurred to one of us that the problem might be solved, indirectly, by making use of a device which, taking the dibromoadipic acids as the example, may be briefly outlined in the following way.

If the ester of either of the dibromoadipic acids (C) and (D) is treated with the sodium derivative of malonic ester, cyclo*pentane*-1 : 2 : 2 : 3-*tetracarboxylic ester* should be produced and this, on hydrolysis and elimination of carbon dioxide, will yield a cyclo*pentane*-1 : 2 : 3-*tricarboxylic acid* :



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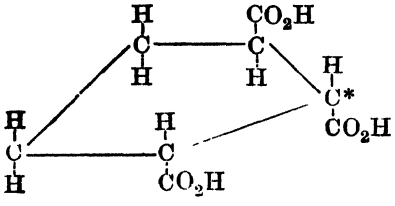
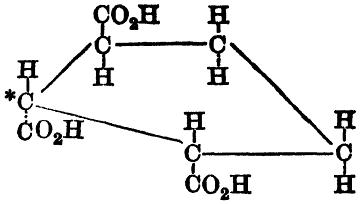
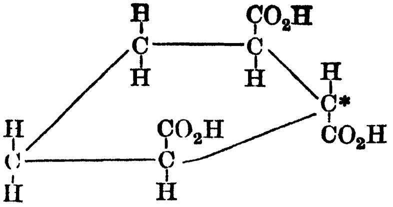
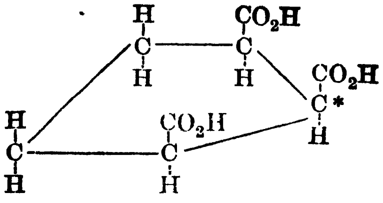
* The substance used melted at 180—182° and consisted essentially of the dibromo-acid (C).

The possible configurations of the acid thus produced are set out in the following table, the $>CH\cdot CO_2H$ derived from the malonic ester synthesis being indicated in each case by *.


(I.)


(II.)


(III.)


(IV.)

Of these configurations, I and II represent the racemic mixture, whereas it is clear that since formulæ III and IV each possess a plane of symmetry they must each represent a non-resolvable *meso*-form.

An examination of the models shows that the racemic form of dibromoadipic acid should ultimately give rise to the resolvable racemic mixture, indicated by the spatial formulæ I and II, whilst the *meso*-form should correspondingly lead to one or both of the non-resolvable substances represented by the formulæ III and IV. It will therefore be clear that the nature of a dibromo-acid may often be conveniently elucidated by studying the products of its interaction with malonic ester, always supposing that no change of configuration accompanies the ring formation.

Such a change is unlikely, because the two carboxyl groups of the dibromoadipic acid, which no doubt take part in the change of configuration which occurs when the dibromo-acid is boiled with alkalis, are protected by conversion into the ethyl ester, and also because the condensation with the sodium derivative of malonic ester takes place rapidly at moderate temperatures and in absolute alcoholic solution.

It thus appears that the process outlined above may be found useful in determining the configuration of other dibromo-acids, such as, for example, the dibromoglutaric acids, and experiments are in progress to determine whether this is the case.

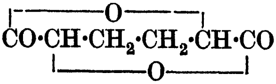
The actual course of the experiments on the condensation of one of the dibromoadipic esters with the sodium derivative of malonic ester may be briefly summarised as follows: The ethyl esters of the two dibromoadipic esters (C, m. p. 193°) and (D, m. p. 139°), have already been prepared and the ester of (C) crystallises well and melts at 66—67°, whereas that of (D) is a syrup.

As the former is so readily obtained pure, it was selected for use and caused to react with the sodium derivative of malonic ester under the conditions detailed on p. 1397. The resulting *ethyl* cyclo*pentane*-1 : 2 : 2 : 3-*tetracarboxylate* distils at 214—216°/23 mm., and, on hydrolysis with alcoholic potassium hydroxide, does not yield, as was to be expected, the corresponding tetracarboxylic acid, but is converted at once, with loss of carbon dioxide, into trans-cyclo*pentane*-1 : 2 : 3-*tricarboxylic acid* (G) of melting point 184—185°. Resolution experiments were now instituted, and it was found that this acid is readily resolved by means of brucine into optically active modifications, of which d-trans-cyclo*pentane*-1 : 2 : 3-*tricarboxylic acid* melts at 126° and has $[\alpha]_D + 72{\cdot}4°$.

It is therefore clear that the acid (G) is the racemic modification corresponding with the configurations I and II in the table on p. 1395.

These facts seem to prove that the dibromoadipic acid (C) of m. p. 193° must be the racemic modification and this acid must correspond with the dihydroxyadipic acid of m. p. 146°, since it is this acid which is resolvable. The *meso*dihydroxyadipic acid of m. p. 174° corresponds therefore with the *meso*dibromoadipic acid of m. p. 139°.

One of the characteristics of the *racemic* dihydroxy-acid (m. p. 146°) is the readiness with which it yields a *dilactone*,


$$\overset{\text{O}}{\overline{\text{CO·CH·CH}_2\text{·CH}_2\text{·CH·CO}}}\underset{\text{O}}{}$$

(Le Sueur, *loc. cit.*, p. 721), and this is in accordance with what would be expected from an examination of the model of its configuration.

On the other hand, the *meso*-dihydroxy-acid (m. p. 174°) should exhibit no such tendency, and this is in accordance with experiment.

It is interesting to note that, on heating *trans-cyclo*pentane-1 : 2 : 3-tricarboxylic acid (G) with acetic anhydride at 150°, it is converted into a much more soluble *cis*-isomeride (H) of m. p. 170° (p. 1399).

Reference to models shows that there are two possible changes of configuration of the acid (G), namely, those which lead to formulæ III and IV respectively (p. 1395). The acid (H) should accordingly be directly derivable from the *meso*-form of dibromoadipic ester by interaction with the sodium derivative of malonic ester, and experiments are in progress with the view of testing this assumption.

NOTE.—Since this paper was written, Dr. C. K. Ingold has been good enough to send me a proof of his paper "The Conditions underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part II," * in which he discusses the configuration of the dibromoadipic acids. As the result of the examination of an interesting series of changes, which the acid of m. p. 193° undergoes, he draws a conclusion contrary to that arrived at in the present communication and considers that this acid is the *meso*-variety. After consulting with Dr. Ingold, it appeared wisest to submit the two papers for publication, so that the facts may be available for discussion. An attempt, which has been made by me, to resolve the dibromoadipic acid of m. p. 193° by means of morphine (compare McKenzie, T., 1912, **101**, 1196) has not been successful because of the ease with which the acid loses hydrogen bromide on treatment with morphine even in the cold.—W. H. P.

EXPERIMENTAL.

Ethyl cyclo*pentane*-1 : 2 : 2 : 3-*tetracarboxylate.*

In the preparation of this ester, sodium (2·3 grams), dissolved in alcohol (50 c.c.), which had been distilled over calcium, was cooled, mixed with ethyl malonate (16 grams) and then ethyl dibromoadipate (17 grams) dissolved in alcohol (50 c.c.) introduced. Sodium bromide separated immediately and heat enough was developed to raise the alcohol to the boiling point. After being heated under reflux for twenty minutes, the product, which was quite neutral, was diluted with water, extracted with ether, the ether evaporated, and the residue distilled in steam, when a little unchanged ethyl malonate passed over. After again extracting with ether and drying over calcium chloride, the oil was distilled under reduced pressure, when most of it boiled at 214—216°/23 mm.

Owing to the fact that the oil contained traces of bromine, the analytical results were unsatisfactory (Found : C = 54·8 ; H = 7·0. $C_{17}H_{26}O_8$ requires C = 56·9 ; H = 7·2 per cent.).

dl-trans-cyclo*Pentane*-1 : 2 : 3-*tricarboxylic Acid.*

This acid is readily obtained when ethyl *cyclo*pentane-1 : 2 : 2 : 3-tetracarboxylate is digested for four hours with one and a half times the calculated quantity of methyl-alcoholic potassium hydroxide (25 per cent.). The product is mixed with water, evaporated until quite free from methyl alcohol, acidified with excess of hydrochloric acid, evaporated to dryness, and the mass extracted with ether in a Soxhlet apparatus. On distilling off the ether, a gum was left which soon crystallised and, after contact with porous porcelain, the nearly colourless residue was crystallised from dilute hydrochloric acid (Found: C = 47·3; H = 5·1. $C_8H_{10}O_6$ requires C = 47·5; H = 4·9 per cent.).

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* This paper has since appeared (this vol., p. 951).

On titration with $N/10$-NaOH, 0·1159 neutralised 17·2 c.c., whereas this amount of a tribasic acid, $C_8H_{10}O_6$, should neutralise 17·3 c.c. This titration and the results of analysis show that the acid is the tribasic acid and not the tetrabasic acid, which might have been expected to result from the hydrolysis of the tetrabasic ester with methyl-alcoholic potassium hydroxide. dl-trans-cyclo*Pentane*-1 : 2 : 3-*tricarboxylic acid* melts at 184—185° and is readily soluble in water, but much less soluble in hydrochloric acid. When it is heated with concentrated hydrochloric acid at 180—200° for two hours, there is very little charring and, on allowing the liquid to concentrate over solid potassium hydroxide in a vacuum, the unchanged *trans*-acid separates and melts at 184—185°.

Resolution of dl-trans-cyclo*Pentane*-1 : 2 : 3-*tricarboxylic Acid.*

This resolution was accomplished in the following manner: The tricarboxylic acid (50 grams) was dissolved in hot water, mixed with precipitated brucine (370 grams), and, after heating on the water-bath, the excess of brucine filtered off with the aid of the pump and well washed. The filtrate and washings were concentrated by distillation from the water-bath under reduced pressure, when, at a certain point, the crystallisation commenced and the distillation was stopped. In a short time, a voluminous separation occurred and the brucine salt was collected while the mass was still warm and several times recrystallised from hot water. After each crystallisation, the rotation was observed, the amount taken being dissolved in 20 c.c. of water and the length of the tube being 2 dcm.

Number of crystallisation.	Weight of substance.	Observed rotation.	$[\alpha]_D$.
1	0·5306	− 1·57°	− 29·58°
2	0·5355	− 1·36	− 25·39
3	0·3648	− 0·80	− 21·92
4	0·3097	− 0·66	− 21·31
5	0·3732	− 0·78	− 20·90
6	0·4071	− 0·85	− 20·87

It therefore appears that the pure brucine salt of the dextro-acid has $[\alpha]_D = 20·87°$. An analysis showed that this salt is formed by the combination of the tribasic acid with three molecules of brucine (Found: N = 6·1. $3C_{23}H_{26}O_4N_2,C_8H_{10}O_6$ requires N=6·1 per cent.).

The pure salt was decomposed by adding ammonia to the warm aqueous solution, the filtrate from the brucine was mixed with excess of hydrochloric acid, and, after evaporating to dryness, the mass was extracted with ether in a Soxhlet apparatus. The gum obtained on distilling off the ether soon solidified, and the *d*-acid was purified by dissolving in dilute hydrochloric acid and leaving over solid potassium hydroxide in a vacuum desiccator, when crystals gradually separated which exhibited the following optical behaviour: 0·2014, dissolved in 20 c.c. of water, gave α_D + 1·46° in a 2-dcm. tube at 15°, whence $[\alpha]_D$ + 72·4°.

d-trans-cyclo*Pentane*-1 : 2 : 3-*tricarboxylic acid* melts at 125—126° (the *dl*-acid melts at 185°) and is readily soluble in water, but much less soluble in concentrated hydrochloric acid.

Attempts were made to obtain the pure *l*-acid from the mother-liquors of the sparingly soluble brucine salt of the *d*-acid, but after several crystallisations from dilute hydrochloric acid the acid melted at 120—125° and had $[\alpha]_D$ − 65·4°; it therefore still contained traces of the *d*-modification.

cis-cyclo*Pentane*-1 : 2 : 3-*tricarboxylic Acid.*

As stated in the introduction, this acid is formed when the *trans*-acid (G) is heated with acetic anhydride. The pure *trans*-acid (2·8 grams) was heated in a sealed tube with acetic anhydride (23 c.c.) for three hours at 150° and the acetic acid and anhydride were distilled off under reduced pressure. The addition of water to the residue caused the anhydro-acid to separate as a heavy layer, but on heating on the water-bath a clear solution was soon formed and this was allowed to concentrate over potassium hydroxide in a vacuum desiccator. Gradually thick, sugar-like crystals separated, and these were recrystallised from dilute hydrochloric acid (Found: C = 47·3; H = 5·2. $C_8H_{10}O_6$ requires C = 47·5; H = 4·9 per cent.).

cis-cyclo*Pentane*-1 : 2 : 3-*tricarboxylic acid* melts at 169—170° and is more readily soluble in water or hydrochloric acid than the corresponding *trans*-acid. A mixture of about equal amounts of the *cis*- and *trans*-acids melts at 145—150° approximately.

The authors wish to thank Mr. T. V. Barker for valuable suggestions made during the course of this investigation.

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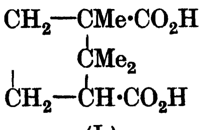
[*Received, July* 21*st*, 1921.

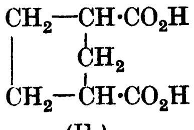
CLXI.—*Resolution of* dl-trans-cyclo*Pentane*-1 : 3-*dicarboxylic Acid.*

By William Henry Perkin, jun., and Harold Archibald Scarborough.

The structural formula of camphoric acid (I) represents this acid as the 1 : 2 : 2-trimethyl derivative of *cyclo*pentane-1 : 3-dicarboxylic acid (II):

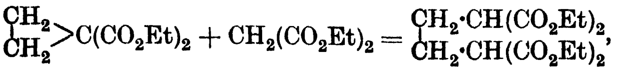


(I.)

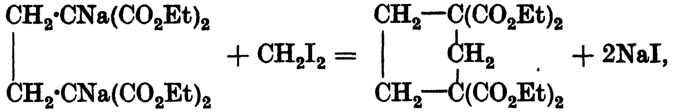


(II.)

The latter acid may therefore be considered as the parent acid or norcamphoric acid, from which camphoric acid is derived by the introduction of three methyl groups. Owing to the importance which attaches to the chemistry of camphoric acid and to the great variety of changes which it undergoes on treatment with reagents, it occurred to one of us (P.) in 1898 that it was a matter of interest to attempt to synthesise the parent acid and to carry out a comparison of its properties with those of camphoric acid. Some years previously (Perkin, T., 1894, **65**, 578) it had been shown that ethyl butanetetracarboxylate, $(CO_2Et)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2$, is produced together with ethyl *cyclo*propanedicarboxylate when ethylene chloride reacts with the sodium derivative of ethyl malonate, but the yield was small, and it was not until Bone and Perkin (T., 1895, **67**, 112) had made the curious observation that ethyl *cyclo*propanedicarboxylate readily reacts with the sodium derivative of ethyl malonate with the formation of ethyl butanetetracarboxylate,



that the latter ester became available in sufficient quantity for synthetical work. As the result of the experience of other syntheses for which ethyl butanetetracarboxylate had been employed with success, the investigation of the action of methylene iodide on the disodium derivative was taken in hand, since it seemed likely that, owing to the well-known ease of formation of the *cyclo*pentane ring, the reaction would proceed normally with the formation of ethyl *cyclo*pentane-1 : 1 : 3 : 3-tetracarboxylate,



$$\begin{array}{l} CH_2{\cdot}CNa(CO_2Et)_2 \\ | \\ CH_2{\cdot}CNa(CO_2Et)_2 \end{array} + CH_2I_2 = \begin{array}{l} CH_2{-}C(CO_2Et)_2 \\ |\quad\ \ CH_2 \\ CH_2{-}C(CO_2Et)_2 \end{array} + 2NaI,$$

which, on hydrolysis and elimination of carbon dioxide, would yield *cyclo*pentane-1 : 3-dicarboxylic acid (II), the parent of camphoric acid.

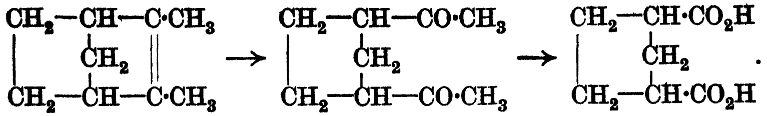
While this investigation was in progress, a paper appeared (*Ber.*, 1898, **31**, 1950) by K. T. Pospischill describing the synthesis of the stereoisomeric 1 : 3-pentamethendicarboxylic acids (*cyclo*pentane-1 : 3-dicarboxylic acids) by the method outlined above. A comparison of the results described by Pospischill with those obtained by the one of us showed such close agreement that there was no object in publishing the work, and the investigation which had been planned was accordingly given up for the time.

As Pospischill had observed, the interaction of methylene iodide with the sodium derivative of ethyl butanetetracarboxylate affords a good yield of ethyl *cyclo*pentane-1 : 1 : 3 : 3-tetracarboxylate, a viscid oil which decomposes on distillation under reduced pressure.

On hydrolysis, this yields the tetracarboxylic acid which melts at 188°, at which temperature it is decomposed with elimination of carbon dioxide and formation of a mixture of the *cis-* and *trans-*modifications of *cyclo*pentane-1 : 3-dicarboxylic acid which melt at 121·5° and 88·5° respectively and are almost impossible to separate by recrystallisation from any solvent.

Pospischill converted the mixed stereoisomeric acids into the anhydride of the *cis*-acid (m. p. 161°) by heating with acetic anhydride and subsequent distillation and from this the *cis*-acid (m. p. 121·5°) was readily obtained by boiling with water. The *trans*-acid (m. p. 88·5°) was prepared from the *cis*-isomeride by heating with hydrochloric acid in a sealed tube at 180°. Pospischill makes no mention of the relationship of these acids to camphoric acid, but describes a number of derivatives and gives conductivity measurements.

It is interesting to note that in 1908 (*Ber.*, **41**, 386) Semmler obtained *trans*-*cyclo*pentane-1 : 3-dicarboxylic acid, unmixed with the *cis*-acid, by oxidising santene, C_9H_{14} (from sandalwood oil), with ozone or permanganate to the diketone, $C_9H_{14}O_2$, and then acting on this with hypobromite, a series of changes which he represents as follows :



The principal object of the present investigation was the resolution of *dl-trans-cyclo*pentane-1 : 3-dicarboxylic acid in order that it might be possible to compare the rotation of the active acid with that of camphoric acid, and as we were unable to obtain santene—which is possibly the most convenient source of this acid—we were obliged to synthesise the acid from ethyl butanetetracarboxylate in the way outlined above. As, however, the preparation of any quantity of the *trans*-acid from the *cis*-acid by heating with hydrochloric acid in sealed tubes is a very laborious process, we endeavoured to modify the method of Pospischill so as to obtain the *trans*-acid direct from the product of the action of heat on the tetracarboxylic acid, and ultimately with success. The mixture of *cis*- and *trans*-acids remaining was first esterified and the mixed esters were purified by fractional distillation (b. p. 150°/22 mm.) and hydrolysed. The colourless mass of the mixed acids was left in contact with acetyl chloride in the cold (p. 1405), when the *cis*-acid was readily converted into the anhydride, whereas the *trans*-acid remained unchanged, and, in this simple manner, considerable quantities of the *trans*-acid were prepared in a pure state.

The resolution of *dl-trans-cyclo*pentane-1 : 3-dicarboxylic acid is very readily accomplished with the aid of brucine, and the salt which first separates is the brucine salt of the *d*-acid and has $[\alpha]_D - 29{\cdot}4°$.

From this salt, *d-trans-cyclo*pentane-1 : 3-dicarboxylic acid is obtained by decomposition with ammonia and was found to melt at 93·5° and have $[\alpha]_D + 5{\cdot}86°$. The mother-liquors of the brucine salt of the *d*-acid yielded *l-trans-cyclo*pentanedicarboxylic acid in an almost pure condition (p. 1406); it melted at 93° and exhibited the rotation $[\alpha]_D - 5{\cdot}29°$.

The value $[\alpha]_D + 5{\cdot}86°$ is much smaller than that exhibited by *d*-camphoric acid, which has $[\alpha]_D + 49{\cdot}7°$, so that the introduction of three methyl groups into the molecule of *d-trans-cyclo*pentane-1 : 3-dicarboxylic acid has the effect of raising the rotation 44°. Experiments are in progress on the resolution of apocamphoric acid (*gem*-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid), and it will be interesting to ascertain what influence the introduction of the *gem*-dimethyl group into the parent acid has on the rotation. It is also interesting to observe that the rotation of *d-trans-cyclo*pentane-1 : 3-dicarboxylic acid is much smaller than that of any other of the fully saturated cyclic dibasic acids which have so far been examined, as the following table shows :

Dicarboxylic acid.	Rotation of *d*-acid.	Active.	Inactive.
*cyclo*Propane-1 : 2-	+ 84·5°	175°	175°
*cyclo*Pentane-1 : 2-	+ 84·4	181	160
*cyclo*Hexane-1 : 4-	+ 18·2	180	215
Camphoric acid	+ 49·7	187	204
*cyclo*Pentane-1 : 3-	+ 5·9	93	88

The table also shows the melting points of the active and inactive acids.

Another point of interest arises from the comparison of the melting points of the *cis*- and *trans*-modifications of *cyclo*pentane-1 : 3-dicarboxylic acid with those of similar (glutaric) type as well as with those of the 1 : 2-(succinic) and 1 : 4-(adipic) types.

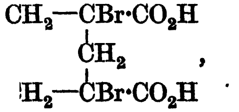
	1 : 3-Dicarboxylic acids.	
	cis-.	*trans*-.
*cyclo*Pentane-	121°	87°
*cyclo*Hexane-	162	119
Apocamphoric acid	204	188
Camphoric acid	208	191

	1 : 2- and 1 : 4-Dicarboxylic acids.	
	cis-.	*trans*-.
*cyclo*Propane-1 : 2-	135°	175°
*cyclo*Butane-1 : 2-	135	170
*cyclo*Pentane-1 : 2-	140	160
*cyclo*Hexane-1 : 2-	192	215
*cyclo*Hexane-1 : 4-	161	300

These tables show that, in the case of the 1 : 3-type, the *cis*-acid always melts at a higher temperature than the corresponding *trans*-acid, whereas in acids of the 1 : 2- or 1 : 4-type the reverse is the case.

Other instructive comparisons of melting points and of ionisation constants of cyclic dibasic acids with those of acids of the $C_nH_{2n}(CO_2H)_2$ series, which result from them by the addition of two atoms of hydrogen, reveal curious relationships which are well worth careful consideration, but the discussion of these would take up too much space in the present communication.

Included in this communication is an account of the formation of *cis*-1 : 3-dibromo*cyclo*pentane-1 : 3-dicarboxylic acid,



$$\begin{array}{l} CH_2{-}CBr{\cdot}CO_2H \\ \quad\;\; CH_2 \\ CH_2{-}CBr{\cdot}CO_2H \end{array},$$

from the acid chloride of *cis*-*cyclo*pentane-1 : 3-dicarboxylic acid by bromination and decomposition with formic acid. It melts at

184° and yields an oily dimethyl ester distilling at 170°/20 mm. The main object in preparing this acid was to endeavour to convert it into the doubly unsaturated acid by removal of two molecules of hydrogen bromide, but although a number of experiments on the action of methyl-alcoholic potassium hydroxide or diethylaniline on the acid and its methyl ester were instituted, it has so far not been found possible to isolate the unsaturated acid.

EXPERIMENTAL.

trans-cyclo*Pentane*-1 : 3-*dicarboxylic Acid.*

The first stage in the preparation of this acid was the conversion of ethyl butanetetracarboxylate (Perkin, T., 1894, **65**, 578; Bone and Perkin, T., 1895, **67**, 112) into *cyclo*pentane-1 : 1 : 3 : 3-tetracarboxylate (p. 1401) by treating the disodium derivative with methylene iodide * under the conditions employed by Pospischill (*Ber.*, 1898, **31**, 1951). A second series of experiments showed that methylene bromide may be used with advantage in the place of the iodide. The preparation of *trans-cyclo*pentane-1 : 3-dicarboxylic acid from the product of this reaction is more conveniently carried out under the following conditions than in the way recommended by Pospischill. The crude ethyl *cyclo*pentanetetracarboxylate, obtained by the addition of water, is extracted twice with ether, the ethereal solution washed, dried, evaporated, and the residual oil, in quantities of 50 grams, hydrolysed by boiling for two hours under reflux with sodium hydroxide (34 grams) dissolved in alcohol (250 c.c. of 80 per cent.). The product is evaporated with water until free from alcohol, decomposed with excess of concentrated hydrochloric acid (150 c.c.), and the water and hydrochloric acid are distilled off under reduced pressure from the steam-bath. The residue is then mixed with sand, thoroughly dried, and the acid extracted with ether, free from alcohol, in a Soxhlet apparatus. After washing with a little bisulphite to remove iodine, the ethereal solution is dried, evaporated, and the residue heated at 170—180° until the evolution of carbon dioxide has ceased. The mixture of the anhydride of *cis-cyclo*pentane-1 : 3-dicarboxylic acid and the free *trans*-isomeride is now esterified by boiling with six times its weight of 10 per cent. alcoholic sulphuric acid for six hours, water is added, the ester extracted with ether, the ethereal solution washed with water and dilute sodium carbonate solution, dried over calcium chloride, and the ether distilled off.

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* The methylene iodide was prepared from methylene chloride and sodium iodide under the conditions given on p. 1408.

On fractioning the crude oily ester under reduced pressure (20 mm.) most of it passed over at 150—160°, leaving a considerable residue of high b. p., and on refractioning, a colourless oil distilled at 148—150°/22 mm. and consisted of the ester of the mixed *cis*- and *trans-cyclo*pentane-1 : 3-dicarboxylic acids (Found : $C = 61{\cdot}5$; $H = 8{\cdot}4$. $C_{11}H_{14}O_2$ requires $C = 61{\cdot}6$; $H = 8{\cdot}4$ per cent.).

When this ester was hydrolysed by boiling with excess of alcoholic potassium hydroxide, a quantity of a crystalline potassium salt separated and it was at first thought that this might be the salt of the *trans*-acid, but examination showed that it also contained the *cis*-modification. The whole was evaporated with water until free from alcohol, acidified, and the acid repeatedly extracted with ether in the usual way, when a nearly colourless syrup was obtained which quickly crystallised.

The weight of these mixed acids was about 47 per cent. of that demanded by theory, calculated on the ethyl butanetetracarboxylate used.

Separation of cis- *and* trans-cyclo*Pentane*-1 : 3-*dicarboxylic Acids.*

The carefully dried mixed acids (20 grams) are shaken with freshly distilled acetyl chloride (25 grams) in the cold, and, after twenty-four hours, the excess of acetyl chloride is removed by allowing the mixture to stand over solid sodium hydroxide in a vacuum desiccator. When the residue is rubbed with dry ether, the anhydride of the *cis*-acid (4 grams) remains undissolved and is filtered off and washed with a little ether. The filtrate, on evaporation, deposits an almost colourless syrup (15 grams) which soon solidifies, and this is again treated with acetyl chloride and yields a further small quantity (0·3 gram) of the *cis*-anhydride. The solid obtained after this second treatment was left in contact with porous porcelain until quite dry; it then melted at 85—86°, whereas the melting point of the pure *trans*-acid, according to Pospischill (*loc. cit.*, p. 1954), is 87—88·5°.

d- *and* l-trans-cyclo*Pentane*-1 : 3-*dicarboxylic Acids.*

The resolution of *dl-trans-cyclo*pentane-1 : 3-dicarboxylic acid is readily accomplished by mixing the acid (15 grams) with brucine (90 grams) and adding the mixture to boiling water, when solution rapidly occurs. The hot filtrate from the excess of brucine almost immediately begins to deposit crystals of the brucine salt of the *d*-acid and, after remaining for some hours, the salt is collected and recrystallised three times from water. After each crystallisation, the rotation was observed in a 2-dcm. tube, the substance being dissolved in each case in 20 c.c. of alcohol.

Number of crystallisation.	Weight of substance.	Observed rotation.	$[\alpha]_D$.
2	0·4558	− 1·37°	− 30·08°
3	0·4231	− 1·25	− 29·54

A small quantity of the third crop was twice recrystallised from hot water without any appreciable alteration in the rotation. If the hot solution is allowed to cool slowly, the salt separates in brilliant, flat needles which effloresce in a desiccator and become somewhat discoloured if dried in the steam oven. The air-dry salt melted at about 127° (Found: C = 57·2; H = 7·5; N = 5·1. $2C_{23}H_{26}O_4N_2,C_7H_{10}O_4,9H_2O$ requires C = 57·4; H = 7·5; N = 5·1 per cent.).

The brucine salt was now dissolved in hot water, the alkaloid precipitated with ammonia, and the filtrate and washings were concentrated by distillation under diminished pressure from the steam-bath. After removing a little brucine which had separated, the solution was further concentrated, acidified, and repeatedly extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and the ether distilled off, when an almost colourless syrup remained which soon solidified.

In this condition, d-trans-cyclo*pentane*-1 : 3-*dicarboxylic acid* melted at about 86°, but after recrystallisation from carbon tetrachloride the melting point rose to 93·5°. On titration, 0·1724 neutralised 0·0872 NaOH, whereas this amount of an acid, $C_5H_8(CO_2H)_2$, should neutralise 0·0873 NaOH. Rotation: 1·0081, dissolved in 20 c.c. of water, gave, in a 2-dcm. tube, the rotation + 0·59°, whence $[\alpha]_D = +5·86°$.

The *ethyl* ester, $C_5H_8(CO_2Et)_2$, was prepared by boiling the acid with 10 per cent. alcoholic sulphuric acid for four hours. It distilled at 145°/20 mm. and 1·2583 dissolved in 20 c.c. of alcohol gave, in a 2-dcm. tube, the rotation + 0·63°, whence $[\alpha]_D = +5·01°$.

l-trans-cyclo*Pentane*-1 : 3-*dicarboxylic Acid.*—In order to isolate this acid, the filtrates and washings of the brucine salt of the *d*-acid were concentrated by distillation under diminished pressure from the steam-bath to about a third, when, on long standing in the ice chest, a small crop of crystals separated which we found to consist of the impure brucine salt of the *d*-acid. The filtrate from these was again evaporated under reduced pressure to about a third, when a larger crop of crystals separated which still contained some of the salt of the *d*-acid. The filtrate from this impure salt of the *l*-acid was made alkaline with ammonia, filtered, and the acid isolated by concentrating the ammonium salt to a small bulk, acidifying with hydrochloric acid, and repeatedly extracting with ether, in the manner described in detail in the case of the isolation of the *d*-acid. The l-trans-cyclo*pentane*-1 : 3-*dicarboxylic acid* thus obtained was left in contact with porous porcelain until quite free from oily impurity, and after twice crystallising from carbon tetrachloride melted at 90—93°. Rotation: 1·0016, dissolved in 20 c.c. of water, gave in a 2-dcm. tube the rotation — 0·53°, whence $[\alpha]_D = -5{\cdot}29°$.

cis-1 : 3-*Dibromo*cyclo*pentane*-1 : 3-*dicarboxylic Acid.*

In preparing this interesting acid, the *cis-cyclo*pentane-1 : 3-dicarboxylic acid (m. p. 121°; 5 grams) obtained by the hydrolysis of the anhydride (p. 1405) was mixed with phosphorus pentachloride (20 grams) and warmed on the steam-bath until evolution of hydrogen chloride had ceased. Bromine (15 grams) was then added and the whole heated for several hours on the steam-bath. The product was mixed with anhydrous formic acid (30 c.c.) and heated until decomposition was complete, when, on standing in the ice chest, the dibromo-acid (8 grams) was deposited as a crystalline crust and after recrystallisation from formic acid melted at 184° (Found: Br = 50·6. $C_7H_8O_4Br_2$ requires Br = 50·6 per cent.).

The *methyl* ester, $C_5H_6Br_2(CO_2Me)_2$, was prepared by gradually adding the dibromo-acid-chloride, prepared as described above, to well-cooled methyl alcohol and allowing to remain for twenty-four hours. On diluting with water, a heavy oil separated which was extracted with ether, the ethereal solution was washed with water and dilute sodium carbonate solution and dried over calcium chloride. After distilling off the ether, the crude methyl ester was purified by distillation under reduced pressure, when it passed over at about 170°/20 mm. as a nearly colourless oil which did not crystallise (Found: C = 32·0; H = 3·5; Br = 45·9. $C_9H_{12}O_4Br_2$ requires C = 31·4; H = 3·4; Br = 46·5 per cent.).

Various attempts were made to obtain the unsaturated acid from the dibromo-acid and its methyl ester, but without success. The methyl ester is scarcely decomposed by heating with diethylaniline on the steam-bath, and even at 150° there is little action, but at higher temperatures a vigorous decomposition sets in with the formation of much tar.

When the methyl ester is added to boiling alcoholic potassium hydroxide, potassium bromide separates, the solution becomes deeply coloured, and again a quantity of tar is produced.

Preparation of Methylene Iodide from Methylene Chloride.

As considerable quantities of methylene iodide were required for the present research and for other purposes and this substance could not be obtained during the war, experiments were made on its preparation from methylene chloride by decomposition with sodium iodide.

A series of experiments on the interaction in methyl-alcoholic solution at various temperatures gave very poor yields, but when the methyl alcohol was replaced by acetone much better results were at once obtained and the following process was ultimately found to work well:

Methylene chloride (30 grams) is mixed with sodium iodide (120 grams) and warm acetone (100 c.c.) and heated in a soda-water bottle for ten hours; the bottle is then re-corked and the heating continued for a further ten hours. After standing overnight, the acetone solution is decanted from the sodium chloride, the latter washed with acetone, and the acetone distilled off; water is then added and the crude methylene iodide extracted with ether. The ethereal solution contains iodine and is washed with water containing sodium hydrogen sulphite, dried, and the ether distilled off. The residue is then fractionated under reduced pressure, when, after a little methylene chloro-iodide has passed over, methylene iodide distils at about 150°/300 mm., the yield being at least 60 per cent. of the possible. If the recovered acetone, containing methylene chloride, is employed in a subsequent operation, the yield is about 10 per cent. higher.

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CLXII.—*The Mechanism of the Oxidation of Drying Oils as Elucidated by a Study of the True Oxygen Absorption. Part II. Linolenic and Linolic Acids.*

By Samuel Coffey.

Linseed oil consists of mixed glycerides of stearic, palmitic, myristic, arachidic, oleic, linolic, and α-linolenic acids, and it is to the last two that linseed oil owes its property of "drying."

In Part I (this vol., p. 1152) it was shown that the true oxygen absorption of linseed oil is apparently in no simple way connected with the iodine value, and also that the free unsaturated acids are oxidised in precisely the same way as the glycerides. The results obtained with the oil or with the free acids are too complex to allow of any satisfactory explanation and, as no relationship exists between the other constants of the oil and the oxygen absorption, it seemed highly probable that the two "active" constituents of linseed oil oxidise differently. The problem was therefore attacked further by studying the oxidation of linolenic and linolic acids.

Linolic acid has never yet been obtained in a pure state, as it occurs naturally. In the case of linolenic acid, Erdmann (*Zeitsch. physiol. Chem.*, 1911, **74**, 179) claims to have isolated the pure α-acid as it occurs in linseed oil, but all the author's attempts to repeat Erdmann's experiments have failed (this vol., p. 1306). This difficulty has been overcome, however, by making use of the fact that hexabromostearic acid on treatment with zinc gives a mixture of stereoisomeric α- and β-acids (Erdmann and Bedford, *Ber.*, 1909, **42**, 1324), from which the α-acid can be separated as hexabromostearic acid by rebromination. To find how α-linolenic acid oxidises, the α- and β-mixture was oxidised as described in Part I; another portion of the same acid mixture was brominated according to the Hehner-Mitchell method and, after the insoluble hexabromostearic acid had been separated, the residual β-acid bromide was debrominated and the β-linolenic acid oxidised under identical conditions. From the difference, which was due to the removed α-acid, the results of the oxidation of α-linolenic acid were obtained.

The oxidation of naturally occurring linolic acid was obtained from a study of the oxidation of a sample containing 10 per cent. of linolenic acid obtained during an attempt to repeat Erdmann's preparation of linolenic acid.

EXPERIMENTAL.

α- and β-Linolenic Acids.

This mixture was obtained by heating carefully purified hexabromostearic acid with 95 per cent. alcohol and zinc dust. The mixed acids were obtained as a pale yellow oil, $d_4^{16} = 0{\cdot}910$. When they were oxidised in the apparatus already described, the results given in Table I were obtained; it is known that the oxidation of α-linolenic acid is complete at the end of six hours. The results are also given graphically in Fig. 1.*

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* The curve for the β-acid represents the amount of oxygen absorbed by the β-acid present in the α + β-mixture, namely, 76·9 per cent., in order to obtain the curve for the α-acid by difference.

TABLE I.

α + β- and β-Linolenic acids. Time of oxidation = six hours.

Acid.	Weight of acids. Gram.	Percentage oxygen absorption.
α + β-mixture	0·2312	41·5
	0·2340	41·5
	0·2340	41·5
β-acid	0·1910	38·55
	0·1803	38·5

FIG. 1.

Linolenic acids.

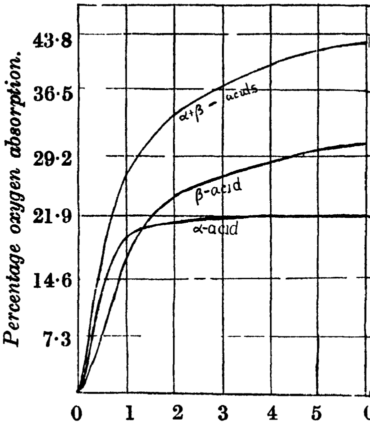
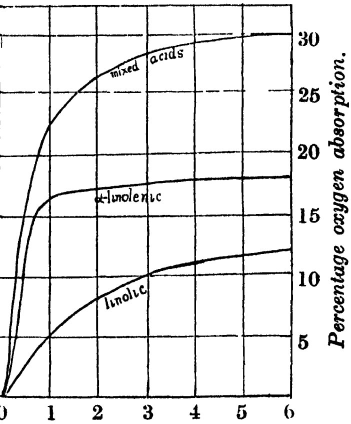


FIG. 2.

Analysis of fatty-acids reaction curve.



Time in hours.

The results of the estimation of the volatile products are given along with those of the β-acid in Table II.

β-*Linolenic Acid.*

For the preparation of this acid a portion of the mixed acids (see above) was brominated in acetic acid and ether and the precipitated hexabromide washed and dried; 2·3970 grams of the α + β-mixture gave 1·5106 grams of $C_{18}H_{30}O_2Br_6$, corresponding to 23·1 per cent. of α-linolenic acid (Erdmann gives 23 per cent.). The filtrate and washings were then evaporated, the oily residue was dissolved in acetic acid and the β-linolenic acid regenerated by boiling the solution with zinc dust for four hours. It is known that this process regenerates only the original β-acid. The results obtained with the β-acid are given in Tables I and II.

TABLE II.

Volatile Products.

Acid.	Weight. Gram.	$BaCO_3$.	Total c.c. of $N/10$-$Ba(OH)_2$.	Percentage of CO_2.	Percentage of oxygen	
					as CO_2.	as CO_2H.
$\alpha + \beta$	0·3036	0·0920	15·3	6·75	4·9	6·4
,,	0·3036	0·0932	15·5	6·84	5·0	6·3
,,	0·3036	0·0928	15·4	6·80	4·95	6·3
β	0·3480	0·0721	11·8	4·62	3·36	4·2

The volatile products, as was observed in Part I, were evolved only after about half an hour, that is, in the later stages of the reaction.

Linolic Acid.

During the attempt to repeat Erdmann's preparation of α-linolenic acid a product containing about 10 per cent. of linolenic acid and 90 per cent. of linolic acid was obtained. The sample on complete oxidation absorbed 27·1 per cent. of oxygen and very little acidic volatile products were formed, a fact which shows that the latter are due solely to the oxidation of linolenic acid.

The Mechanism of the Oxidation of α-Linolenic Acid.

From the results obtained with the mixture of α- and β-acids and with the β-acid alone, the oxygen absorbed by the α-acid during oxidation can be obtained as follows.

One hundred grams of the mixture contained 23·1 grams of α- and 76·9 grams of β-acid and absorbed 41·5 grams of oxygen. Since 76·9 grams of β-acid absorb 29·6 grams of oxygen, therefore, by difference, 23·1 grams of α-acid absorb 11·9 grams of oxygen, and 100 grams absorb 51·4 grams of oxygen. This corresponds almost exactly with 9 atoms of oxygen per molecule of α-linolenic acid ($C_{18}H_{30}O_2 + 9O$ requires 51·8 per cent.).

From the above estimations it is seen that the acidic volatile products come from the linolenic acid only; further, it has been shown in Part I (*loc. cit.*, p. 1158) that the ratio $CO_2 : CO_2H = 1 : 1$ and that the ratio of the *excess* of oxygen above that required for a simple molecular oxidation (*loc. cit.*, p. 1160), which is due to the reaction of the extra three atoms of oxygen with the α-linolenic acid, to the oxygen in the volatile products is 3 : 4.

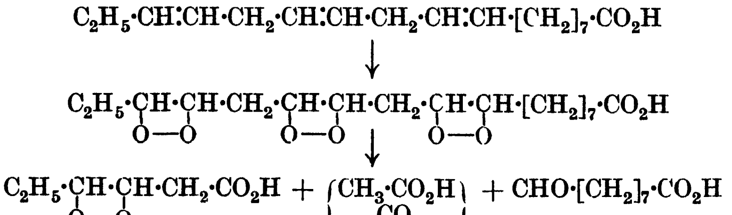
Also, from the results given in Table II, the difference in volatile acids as shown by titration is equivalent to 2460 c.c. of $N/10$-baryta per 23·1 grams of α-acid. Therefore, the difference for 1 gram-molecule of α-linolenic acid (278 grams) is 29,650 c.c.

of *N*/10-baryta (2·965 equivalents), which is three equivalents as nearly as could be expected.

The percentage of carbon dioxide evolved from α-linolenic acid calculated from these figures is 14·1, which, considering the small amounts of acids available and the small difference in weight of the barium carbonate expected (equivalent to 0·075 gram of linolenic acid), is in sufficiently good agreement with that required for one molecule of carbon dioxide per molecule of α-acid, namely, 15·8 per cent.

As indicated in Part I, many hypotheses have been put forward to explain the mechanism of the oxidation of linseed oil, but apparently none suggests the idea that the different constituents of the oil oxidise differently.

From the work of previous investigators, notably that of Fahrion and Weger (*Chem. Zeit.*, 1904, **28**, 1196) and Ingle (*J. Soc. Chem. Ind.*, 1913, **32**, 639) it appears that the first process is one of molecular oxidation giving peroxides of type II. These, according to the results recorded above, are further oxidised by the extra three atoms of oxygen, giving, as the main acidic volatile products, carbon dioxide and acetic acid in the ratio 1 : 1. From a consideration of the results given above and in Part I, the oxidation of α-linolenic acid (I) appears to take place according to the following scheme.



$$C_2H_5\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H \qquad (I)$$

$$\downarrow$$

$$C_2H_5\cdot\underbrace{CH\cdot CH}_{O-O}\cdot CH_2\cdot\underbrace{CH\cdot CH}_{O-O}\cdot CH_2\cdot\underbrace{CH\cdot CH}_{O-O}\cdot[CH_2]_7\cdot CO_2H \qquad (II)$$

$$\downarrow$$

$$C_2H_5\cdot\underbrace{CH\cdot CH}_{O-O}\cdot CH_2\cdot CO_2H + \begin{Bmatrix} CH_3\cdot CO_2H \\ CO_2 \end{Bmatrix} + CHO\cdot[CH_2]_7\cdot CO_2H \qquad (III.)$$

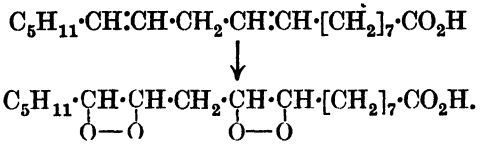
This scheme satisfactorily explains the several ratios found to exist between the acidic volatile products, the *excess* oxidation and the amount of oxygen actually absorbed by the linolenic acid, and, as far as can be ascertained, it explains all the main facts known about the oxidation of this substance and linseed oil. It is only put forward, however, in a tentative manner, because it is felt that the evidence, as far as it goes, is not quite sufficient definitely to establish the mechanism of the oxidation beyond all doubt.

With regard to the small amount of formic acid produced in this oxidation, Wislicenus has recently shown (*Ber.*, 1918, **51**, 942) that carbon dioxide is reduced to formic acid by hydrogen peroxide and it seems conceivable that this might also take place here.

The Mechanism of the Oxidation of Linolic Acid.

The mixture containing about 10 per cent. of linolenic acid and 90 per cent. of linolic acid absorbed 27·1 per cent. of oxygen. As the α-linolenic acid in the mixture accounts for 5·2 per cent. of this, the linolic acid accounts for 21·9 per cent. Therefore the percentage oxygen absorption for linolic acid is 24·4, which corresponds with four atoms of oxygen per molecule (four atoms are equivalent to 23 per cent. and five atoms to 28·5 per cent.).

Further, as the oxidation of linseed oil is primarily one of molecular oxidation, and as linolic acid contains two double linkings and absorbs four atoms of oxygen, in all probability this acid simply oxidises by the addition of a molecule of oxygen to each unsaturated linking, giving as the primary product linolic acid diperoxide.



$$C_5H_{11}\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$$
$$\downarrow$$
$$C_5H_{11}\cdot\underset{O{-}O}{CH\cdot CH}\cdot CH_2\cdot\underset{O{-}O}{CH\cdot CH}\cdot[CH_2]_7\cdot CO_2H.$$

Linoxyn, the tough, resinous oxidation product of linseed oil, is probably a very complex mixture of unchanged saturated glycerides and olein, together with the condensation products of the above primary oxidation products, some of which will have combined with glycerol. It is not surprising, therefore, that all attempts to resolve it into its several constituents have up to the present been unsuccessful.

The Quantitative Composition of Linseed Oil.

Many investigators since the time of Hazura (*Monatsh.*, 1888, **9**, 180; *Zeitsch. angew. Chem.*, 1888, **1**, 302) have attempted to determine the proportions of the constituents in linseed oil (Fahrion, *Zeitsch. angew. Chem.*, 1903, **16**, 1193; 1910, **23**, 1106; Fokin, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 501; Erdmann and Bedford, *Zeitsch. physiol. Chem.*, 1910, **69**, 76). These determinations vary within fairly wide limits, but Friend ("Chemistry of Linseed Oil," 1917, p. 56 *et seq.*) from a consideration of the various data, considers that linseed oil of iodine value 180 has the composition given in the last column of Table III.

The main difficulty seems to be the lack of a satisfactory method of estimating the various constituents when mixed together.

From the results given in this and the previous paper, the constituents in the oil used can be estimated as follows.

The amount of α-linolenic acid can be calculated from the amount of carbon dioxide obtained in the volatile products by multiplying by the ratio $C_{18}H_{30}O_2/CO_2$. The total oxygen absorption is due to the oxidation of linolic and linolenic acids, and since the amount of the latter is known, that of the linolic acid can be calculated. The iodine value gives the total unsaturation, and as the amounts of linolenic and linolic acids are known, that of the oleic acid is obtained by difference. Glycerol is estimated directly, and the only constituents not known by direct estimation are the saturated acids and the unsaponifiable matter. The results of such calculations are given in Table III along with those of Friend.

TABLE III.

Constituents of Linseed Oil.

Constituent.	Percentage.	Iodine value.	Percentage in linseed oil (iodine value 180). (Friend).
Saturated acids and unsaponifiable matter	8·1	0	10
Glyceryl radicle	4·3	0	4·6
Oleic acid	5·0	4·5	5·0
Linolic ,, ...	48·5	86·1	48·3
Linolenic ,, ...	34·1	93·5	32·1
	100·0	184·1	100·0

It will be seen that the amounts of the constituents calculated from the oxygen absorption values are almost identical with those recorded by Friend, and this result may be regarded as strong evidence in support of the views put forward for the mechanism of the oxidation of linolenic and linolic acids.

Analysis of the Oxidation Curves.

The mixed fatty acids in the oil used contain (Table III) 50·7 per cent. of linolic acid and 35·65 per cent. of linolenic acid, which are equivalent to an oxygen absorption of 11·65 and 18·45 per cent. on the mixed fatty acids respectively. If a curve calculated on the unimolecular reaction law, is drawn for the amount of linolic acid calculated from the mixed fatty acid curve (Fig. 2), a curve is obtained identical with that obtained for linolenic acid from the results of experiments on the linolenic acids (Fig. 1).

The fact that this curve (Fig. 2), whilst being derived from a totally different set of experiments, is identical with that in Fig. 1 may also be taken as confirmation of the conclusions already arrived at above. Also, it seems highly probable that the oxidation of linolic acid, excluding the very small induction period, may be represented by a simple logarithmic curve of the form

$$k = \frac{1}{t} \log_e \frac{a}{a - x},$$

as would be expected on theoretical considerations for the simple molecular oxidation.

In the case of linolenic acid, the shape of the reaction curve indicates that two different types of reactions, probably consecutive reactions, are taking place. Hence the curve is not of the simple logarithmic type suggested by several investigators.

The author takes this opportunity to express his great indebtedness to Professor F. S. Kipping, F.R.S., for his constant attention during this work and to the Royal Commissioners for the Exhibition of 1851 for a scholarship which enabled him to carry out this investigation.

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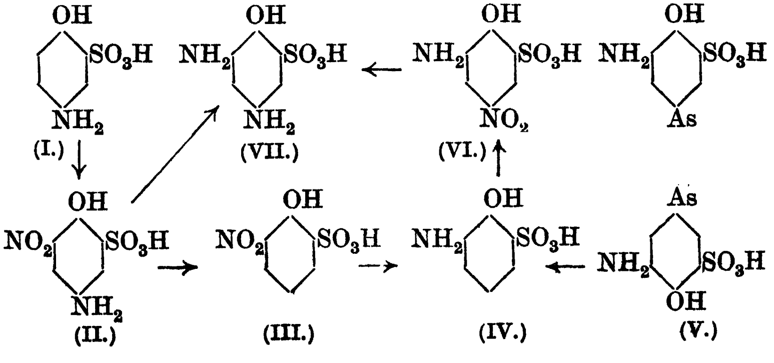
CLXIII.—*Derivatives of Sulphur in Commercial Salvarsan. Part II.*

By HAROLD KING.

THE present communication contains the proof of the constitution of the sulphonic acid 3-amino-4-hydroxy-5-sulphophenylarsinic acid described in Part I (this vol., p. 1109), and isolated either by oxidation of the constituent of salvarsan containing sulphur which is insoluble in methyl alcohol or by oxidation of the acid, $C_6H_8O_6NSAs$, obtained as a by-product in the reduction of 3-nitro-4-hydroxyphenylarsinic acid to 3-amino-4-hydroxyphenylarsinic acid by sodium hyposulphite. On reduction, this sulphonic acid gave the arseno-compound (V), which on hydrolysis gave a new sulpho-acid of *o*-aminophenol (IV).



The proof of the position of the sulpho-group follows from the synthesis by the stages (I) to (IV). Additional confirmation is furnished by the nitration of this 6-aminophenol-*o*-sulphonic acid, obtained by the hydrolysis of the arseno-compound, to 4-nitro-6-aminophenol-*o*-sulphonic acid (VI), which agrees in properties with an acid to which this constitution is assigned, described in D.R.-P. 123611 and obtained by partial reduction of the corresponding dinitro-compound. On reduction of the isomeric compounds (II) and (VI), both yielded the same 4 : 6-diaminophenol-*o*-sulphonic acid (VII).

The difficulty of identifying some of the above compounds from the meagre account in the patent literature has been to some extent remedied by a description of their more distinctive reactions.

In one particular, the author is compelled by subsequent experimental developments to modify the interpretation of certain results given in Part I. The substance $C_6H_8O_6NSAs$, obtained in 10 per cent. yield as a by-product in the reduction of 3-nitro-4-hydroxyphenylarsinic acid by sodium hyposulphite, and described as 3-amino-4-hydroxy-5-sulphinophenylarsinic acid with the reservation expressed in the foot-note (p. 1108) that it might be the isomeric 3-amino-4-hydroxy-5-sulphophenylarsenious acid, has now been prepared by reduction of 3-amino-4-hydroxy-5-sulphophenylarsinic acid by hydrogen iodide and sulphur dioxide, and must therefore be the sulphonic acid of the phenylarsenious acid, and not the sulphinic acid of the phenylarsinic acid. This introduces a welcome simplification into the chemistry of the derivatives of sulphur in commercial salvarsan, as the amorphous arsenobenzenes there described containing the sulphinic acid group are in reality identical with the corresponding sulphonic acids, and the slight differences in analytical figures and toxicities are those of amorphous substances prepared under different experimental conditions.

To summarise, the main sulphur-containing impurity in commercial salvarsan is 3 : 3′-diamino-4 : 4′-dihydroxy-5-sulphoarsenobenzene monohydrochloride, associated with varying proportions of the sulphate of salvarsan base.

EXPERIMENTAL.

Monosulphonation of p-*Nitrophenol.*

Post's process (*Annalen*, 1880, **205**, 38) gave unsatisfactory results. The following modification gives excellent yields. Thirty grams of *p*-nitrophenol were added to 80 c.c. of Nordhausen sulphuric acid (16 per cent. SO_3) at − 10°, and kept at 0° for twenty-four hours. The diluted solution was extracted with ether to remove tar and unchanged *p*-nitrophenol, and the required 4-nitrophenol-*o*-sulphonic acid isolated as the calcium salt.

*Deamination of 6-Nitro-4-aminophenol-*o*-sulphonic Acid* (II). *6-Nitrophenol-*o*-sulphonic Acid* (III).

The calcium salt of 4-nitrophenol-*o*-sulphonic acid was reduced to the amino-compound (I) with tin and hydrochloric acid and the product nitrated as described in D.R.-P. 113337. The yields are excellent. The salient properties of this acid (II) are described below (p. 1419).

The deamination was conducted as follows. 4·7 Grams of 6-nitro-4-aminophenol-*o*-sulphonic acid were diazotised in hydrochloric acid solution. The crystalline diazonium sulphonate which separated was collected by filtration and added to 200 c.c. of absolute alcohol. On addition of copper powder (2 grams), the diazo-nitrogen was evolved without heating. After an hour had elapsed the solution was filtered from undissolved copper, diluted with water, and the alcohol removed under reduced pressure. The copper was precipitated as sulphide and the bright red filtrate concentrated to a small volume, treated with excess of ammonia, and the product isolated as the ammonium salt. The yield was 1·5 grams.

The *ammonium* salt of *6-nitrophenol-*o*-sulphonic acid* is readily soluble in hot water but rather sparingly so in cold. It crystallises anhydrous in long, glistening, delicate, golden leaflets (Found: ammonium N = 5·7; S = 13·8. $C_6H_8O_6N_2S$ requires ammonium N = 5·9; S = 13·6 per cent.). With ferric chloride solution, a wine-red coloration is produced.

Apart from the ammonium salt, the most characteristic salt is the *lead* salt, which crystallises magnificently in orange-yellow prisms with wedge-shaped ends and also in hexagonal plates.

The free *acid*, obtained from the lead salt by decomposition with hydrogen sulphide, crystallises in delicate, pale yellow needles and is very soluble in water. It has no definite melting point, and, unlike the isomeric 4-nitrophenol-*o*-sulphonic acid, it is not extractable by ether and is not precipitated on addition of concentrated hydrochloric acid to the solid ammonium salt.

*6-Aminophenol-*o*-sulphonic Acid* (IV).

The ammonium salt (1·1 grams) of 6-nitrophenol-*o*-sulphonic acid was reduced with tin and hydrochloric acid and the free amino-acid isolated after removal of the tin as sulphide. The yield was 0·9 gram.

This acid proved to be identical with the acid obtained by the hydrolysis by Karrer's method of 3 : 3′-diamino-4 : 4′-dihydroxy-5 : 5′-disulphoarsenobenzene. The identity was proved by the following properties and by a direct comparison with the two other known 6-aminophenol-*m*- or *p*-sulphonic acids.

Both acids crystallise identically, and with one-half a molecule of water of crystallisation, which is lost by air-drying for twenty-four hours under summer conditions of temperature (Found : in the synthetic acid, $H_2O = 4{\cdot}6$. $C_6H_7O_4NS,\frac{1}{2}H_2O$ requires $H_2O = 4{\cdot}5$ per cent. After twenty-four hours' air-drying, loss $= 0{\cdot}5$; $N = 7{\cdot}6$. $C_6H_7O_4NS$ requires $N = 7{\cdot}4$ per cent. Found : for the acid obtained by hydrolysis, $H_2O = 4{\cdot}2$; on air-dried material, $H_2O = 0{\cdot}5$; $N = 7{\cdot}5$ per cent.). Their aqueous solutions in dilute ammonia readily become coloured, and addition of barium chloride precipitates a sparingly soluble barium salt crystallising in rosettes of glistening hexagonal leaflets. Neither of the other known isomeric 6-aminophenol-*m*- or -*p*-sulphonic acids gives an insoluble barium salt (Bennewitz's statement, *J. pr. Chem.*, 1873, [ii], **8**, 51, that the *p*-sulpho-acid gives an insoluble barium salt was not confirmed). Addition of sodium nitrite and hydrochloric acid produces an orange-red solution, becoming paler on further addition of nitrite, and when this reaction mixture is added to alkaline β-naphthol, an insoluble blue dye results. With ferric chloride an intense cherry-red coloration is obtained, the isomeric *m*-sulpho-acid giving an intense indigo-blue.

Nitration of 6-*Aminophenol*-o-*sulphonic Acid.*

6-Aminophenol-*o*-sulphonic acid (1·5 grams), prepared from 3 : 3′-diamino-4 : 4′-dihydroxy-5 : 5′-disulphoarsenobenzene, was dissolved in 6 c.c. of sulphuric acid, cooled to — 5°, and 1·2 c.c. of a mixture of equal volumes of nitric acid (D 1·42) and sulphuric acid were added. After thirty minutes the solution was poured on to ice and the crystalline nitro-compound collected. The yield was 1·6 grams.

This acid crystallises in three forms; a very stable monohydrate crystallising in columns or stout prisms, which only loses its water of crystallisation at 140°. In addition it forms a dimorphous dihydrate. When crystallised from boiling water, the first form which separates is a dihydrate crystallising in long glistening needles. On keeping for a few hours, these slowly pass into solution with deposition of another dihydrate crystallising in flattened, serrated needles or with deposition of the stable monohydrate described above. Both dihydrates lose their water of crystallisation readily at 100° (Found: in monohydrate, $H_2O = 7{\cdot}7$. $C_6H_6O_6N_2S,H_2O$ requires $H_2O = 7{\cdot}7$ per cent. Found: in unstable dihydrate, $H_2O = 11{\cdot}2$; in stable dihydrate, $H_2O = 12{\cdot}1$. $C_6H_6O_6N_2S,2H_2O$ requires $H_2O = 13{\cdot}3$ per cent. Found: in the anhydrous substance, $S = 14{\cdot}0$. $C_6H_6O_6N_2S$ requires $S = 13{\cdot}7$ per cent.).

Properties of 4-*Nitro*-6-*aminophenol*-o-*sulphonic and* 6-*Nitro*-4-*aminophenol*-o-*sulphonic Acids* (VI and II).—These acids are respectively derivatives of *p*- and *o*-nitrophenol and for brevity will be referred to as such.

The *p*-nitro-compound decomposes violently at 285°, in agreement with the statement in D.R.-P. 123611, whereas the *o*-compound is unchanged at 290°. The ammonium salt of the *p*-compound crystallises in diamond-shaped leaflets, that of the *o*-compound in needles; the latter is the more soluble and dissolves with a deeper red colour. The sparingly soluble barium salts crystallise in needles, the salt of the *p*-compound being distinctly the less soluble. The calcium salts are much more soluble. Both acids diazotise and couple with alkaline β-naphthol, the *p*-acid alone forming an insoluble red dye.

Reduction of the Isomeric Nitroamino-compounds to the same 4 : 6-*Diaminophenol*-o-*sulphonic Acid* (VII).—Both the above nitro-amino-acids, on reduction with tin and hydrochloric acid and removal of the tin as sulphide, yield the same monohydrochloride of 4 : 6-diaminophenol-*o*-sulphonic acid (Found: for the diamine from 4-nitro-6-aminophenol-*o*-sulphonic acid, $Cl = 14{\cdot}9$; for the diamine from the isomeric 6-nitro-4-aminophenol-*o*-sulphonic acid, $Cl = 14{\cdot}9$; $N = 11{\cdot}6$. $C_6H_8O_4N_2S,HCl$ requires $Cl = 14{\cdot}7$; $N = 11{\cdot}6$ per cent.).

The identity of the two follows from the following properties. Both monohydrochlorides are readily soluble and crystallise from water in diamond-shaped leaflets. The base from each, when precipitated by a limited amount of sodium hydrogen carbonate, crystallises in microscopic plates or leaflets. In ammoniacal solution, both on addition of barium chloride solution rapidly deposit a sparingly soluble barium salt crystallising in nodules or warts. The calcium salt in both cases is very soluble. The coloration with ferric chloride—a red rapidly deepening to purple—is the same in both cases, as is also the red coloration given by oxidising agents, nitric acid, hydrogen peroxide, and bromine water. When diazotised, both give orange-red solutions rapidly deepening in colour on further addition of nitrite and when added to alkaline β-naphthol both precipitate purple-blue dyes.

Reduction of 3-Amino-4-hydroxy-5-sulphophenylarsinic Acid to the Phenylarsenious Acid.

One gram of the substituted phenylarsinic acid was suspended in 8 c.c. of water and 4·5 c.c. of concentrated hydrochloric acid and 0·25 gram of potassium iodide were added. Sulphur dioxide was passed through the solution for about an hour, when the reduction was complete. The substituted arsenious acid was collected and weighed 0·95 gram.

3-*Amino-4-hydroxy-5-sulphophenylarsenious acid* was identical with the substance erroneously described as 3-amino-4-hydroxy-5-sulphinophenylarsinic acid in Part I (p. 1108) (Found: on dried substance, N = 4·6. $C_6H_8O_6NSAs$ requires N = 4·7 per cent.).

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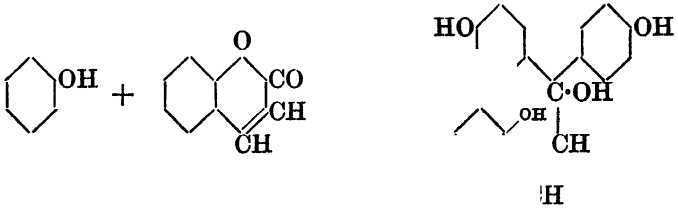
CLXIV.—*Phenolcoumarein and Resorcinolcoumarein.*

By SRI KRISHNA.

PECHMANN (*Ber.*, 1883, **16**, 2119) and other investigators have observed that different products are obtained by condensing malic acid or acetoacetic acid with phenols under different experimental conditions. Such a case is that of resocyanin, to which Wittenberg (*J. pr. Chem.*, 1882, [ii], **26**, 66) gave the formula $C_{21}H_{18}O_6$, and Michael (*Amer. Chem. J.*, 1883, **5**, 434) expressed the same by the formula $C_{10}H_8O_3$.

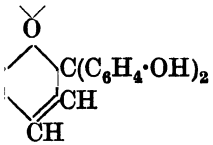
Previous workers, ignoring the other products of reaction, isolated only coumarin and substituted coumarins from the products of the interaction of phenols and malic acid. In this paper it is shown that the condensation can be carried a step further if an excess of phenol and a suitable condensing agent are employed at a suitable temperature. In all cases, since coumarin is the first product of the reaction, the further condensation with phenols was carried out by heating a mixture of coumarin (1 mol.) and phenol (2 mols.) at 120° with zinc chloride in the presence of dry hydrogen chloride (compare this vol., p. 289).

The products of condensation of phenols and coumarins may be of the phenolphthalein type of compound. Since the analytical data point to the presence of an extra molecule of water, it is considered that the product in question may have been formed, as shown below, by the rupture of the lactone ring :



A similar compound was obtained from coumarin dibromide and phenol, in which case the bromine atoms probably migrate from the quadrivalent oxygen atom to the double linking.

Coumarin is known to give various additive compounds, for example, with mercuric chloride and platinic chloride, but phenolcoumarein yields no such products, although the quadrivalent oxygen may still be assumed to be present in the molecule :



Phenolcoumarein gives a tripotassium salt, a trimethyl ether, and a tribenzoyl derivative, but only a diacetyl compound. This may perhaps be accounted for, if it is considered that the acetic anhydride acts also as a condensing agent, eliminating water and reproducing the original lactonic ring. Phenolcoumarein dissolves in alkali hydroxides with a beautiful deep purple colour, which is distinctly noticeable even in very dilute solutions and is destroyed by the addition of a slight excess of acid or an excess of alkali hydroxide. The colour always reappears on neutralisation of the solution, no matter how this has previously been treated. When coumarin is condensed with resorcinol according to the procedure described above, resorcinolcoumarein is formed, the alkaline solution of which shows a strong green fluorescence; analytical data indicate the formula $C_{21}H_{16}O_5,H_2O$. It may be suggested that resocyanin, which Schmidt and Wittenberg found to be a compound of the formula $C_{21}H_{18}O_6$, exhibiting fluorescence in alkaline solution, is the resorcinolcoumarein described above.

EXPERIMENTAL.

Phenolcoumarein.

A mixture of 15 grams of coumarin and 20 grams of freshly distilled phenol, which liquefied with much lowering of the temperature, was heated for two hours at 120° with 10 grams of finely powdered, anhydrous zinc chloride in a current of dry hydrogen chloride. The mixture developed a pink colour, the current of gas was stopped, and the whole mass was heated for another two hours at the same temperature. The colour slowly deepened and ultimately became black towards the end of the reaction. The black mass, while hot, was poured into 500 c.c. of 5 per cent. hydrochloric acid and boiled to remove zinc chloride and excess of phenol. The process was repeated twice, and the solid remaining after filtration was washed with hot water, powdered, made into a thin paste with water, and poured into 500 c.c. of 3 per cent. sodium hydroxide solution. After remaining overnight, the mixture was filtered and the red solution precipitated with dilute hydrochloric or acetic acid, when a brown precipitate was obtained. This was collected, the above process repeated, and for the third time the precipitate was dissolved in sodium carbonate solution and precipitated with dilute hydrochloric acid, when an orange precipitate was obtained, which crystallised from dilute hydrochloric acid as a bright orange, crystalline powder. For analysis, the powder was well washed with water and dried in a vacuum desiccator over sulphuric acid (Found: C = 71·31; H = 5·34. $C_{21}H_{20}O_5$ requires C = 71·59; H = 5·68 per cent.).

Phenolcoumarein obtained in this way is an orange, microcrystalline powder containing one molecule of water. When dried in a steam-oven it darkens and acquires a green lustre, and then melts at 103—105°. It dissolves in alkalis with a pinkish-red colour which changes to pale yellow on the addition of a slight excess of acid. It is almost insoluble in ether, benzene, or chloroform, but dissolves quite readily in alcohol or acetic acid. On heating at 95° in a vacuum over phosphoric oxide, it loses one molecule of water (Found: C = 75·49; H = 5·50. $C_{21}H_{18}O_4$ requires C = 75·45; H = 5·38 per cent.).

The *potassium* salt, $C_{21}H_{13}O_3K_3,H_2O$, was obtained by dissolving molecular proportions of potassium hydroxide and phenolcoumarein in 98 per cent. alcohol. The mixture was heated on a water-bath for a few minutes and filtered after half an hour; the purple filtrate deposited the tripotassium salt as a pink powder on slow evaporation. It dissolved readily in water, giving red solutions, and contained one molecule of water (Found: K = 26·64. $C_{21}H_{15}O_4K_3$ requires K = 26·19 per cent.).

The *silver* salt was obtained as a brown precipitate by heating the calculated weights of silver nitrate and the tripotassium salt in aqueous solution on a water-bath for a few minutes and adding a few drops of dilute nitric acid. The precipitate, after being washed with hot dilute alcohol to remove unchanged phenolcoumarein and silver nitrate, was dried in a steam-oven and kept in a desiccator (Found: Ag = 49·81. $C_{21}H_{15}O_4Ag_3$ requires Ag = 49·44 per cent.).

The *trimethyl* ether, $C_{24}H_{24}O_4$, was prepared by heating an alkaline solution of phenolcoumarein with methyl sulphate in methyl-alcoholic solution on a water-bath for an hour, filtering the cooled mixture into a large quantity of cold water, and faintly acidifying, when the methyl ether was obtained as a brown, flocculent precipitate. After being washed and dried, the brown powder was further purified by dissolving it in a mixture of alcohol and ether (10 per cent. of alcohol) and pouring the filtered solution into a large volume of light petroleum, from which a pale grey powder was obtained. After being washed with ether and dried in a vacuum desiccator, the compound melted at 74° (Found: C = 76·91; H = 6·18. $C_{24}H_{24}O_4$ requires C = 76·59; H = 6·39 per cent.).

The *tribenzoyl* derivative was prepared by shaking phenolcoumarein, dissolved in an alcoholic solution of sodium hydroxide, with the calculated quantity of benzoyl chloride until the smell of the latter was completely lost. After being heated on a water-bath for two hours, the mixture was cooled and filtered into a large excess of water. The brown precipitate obtained was washed with hot water and dried. The tribenzoyl derivative thus obtained was soluble in benzene and chloroform and crystallised by slow evaporation of its solution in a mixture of the two in very small pale grey crystals, which melted at 154° (Found: C = 77·77; H – 5·15. $C_{42}H_{30}O_7$ requires C = 78·02; H = 4·64 per cent.).

The *diacetyl* derivative was prepared by heating 5 grams of phenolcoumarein, 10 grams of acetic anhydride, and 5 grams of sodium acetate for four hours under reflux. The solution was then poured into a large excess of water containing 10 per cent. of alcohol, and heated on a water-bath to decompose the excess of acetic anhydride. The brown, viscous residue obtained became harder after repeated washings, and was then powdered and dried. For analysis, a sample was dissolved in glacial acetic acid and filtered into a large excess of water, when, on slight heating, a brownish-red precipitate was obtained, which was thoroughly washed with luke-warm water and dried in a desiccator over sulphuric acid;

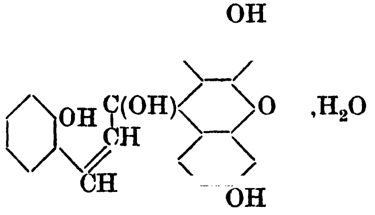
it then melted at 132° (Found: $C = 72{\cdot}11$; $H = 5{\cdot}17$. $C_{25}H_{22}O_6$ requires $C = 71{\cdot}77$; $H = 5{\cdot}26$ per cent.).

Tetrabromophenolcoumarein was prepared by heating 3·2 grams of phenolcoumarein and 3·2 grams of bromine in glacial acetic acid under reflux on a water-bath for two hours. After remaining overnight, the mixture was filtered into a large excess of water, when a pale brown precipitate was thrown down. This was washed thoroughly with hot water to remove acetic acid and excess of bromine and dried. The brown powder was soluble in alcohol or chloroform, but could not be obtained crystalline. A sample was dissolved in ether, the solution filtered into an excess of light petroleum, and the brown powder that was deposited after some time was washed with light petroleum and dried in a vacuum desiccator, when it melted at 172—173° (Found: $Br = 50{\cdot}77$. $C_{21}H_{14}O_4Br_4$ requires $Br = 49{\cdot}22$ per cent. $C_{21}H_{12}O_3Br_4$ requires $Br = 50{\cdot}64$ per cent.).

Phenoldibromocoumarein.

This compound was prepared by heating 10 grams of coumarin dibromide (Perkin, *Annalen*, 1871, **157**, 116) with 8 grams of freshly-distilled phenol and 5 grams of zinc chloride at 105° for four hours in a current of dry hydrogen chloride. The melt was poured into a large volume of dilute hydrochloric acid, heated, and the phenoldibromocoumarein extracted as in the case of phenolcoumarein. *Phenoldibromocoumarein* is a brownish-red powder which gives a pink colour with alkali hydroxides (Found: $C = 51{\cdot}42$; $H = 3{\cdot}96$. $C_{21}H_{16}O_3Br_2$ requires $C = 51{\cdot}04$; $H = 3{\cdot}64$ per cent.).

Resorcinolcoumarein.



This substance was prepared by heating a mixture of 14·6 grams of coumarin, 22 grams of resorcinol, and 10 grams of freshly-fused zinc chloride at 120° in a current of dry hydrogen chloride. After four to five hours, when the reaction was completed, the melt was poured into 500 c.c. of water acidified with 20 c.c. of hydrochloric acid, and the resorcinolcoumarein extracted as in the case of phenolcoumarein. The crude product, a brown powder, was dissolved in alcohol, boiling water added until a turbidity appeared, and the mixture boiled with animal charcoal. The filtered solution was diluted with water, when an orange powder separated. This was collected and washed and again precipitated from an alkaline solution with dilute acetic acid.

The crystalline, orange-yellow powder, which contains a molecule of water, is soluble in alcohol, ether, or acetic acid. The solution in acetic acid fluoresces slightly, whilst the solutions in alkalis exhibit a strong green fluorescence. On heating, the orange powder changes into a dark, crystalline powder with a green lustre and melts at 176—177° (Found: $C = 68{\cdot}59$; $H = 5{\cdot}14$. $C_{21}H_{16}O_5$ requires $C = 68{\cdot}85$; $H = 4{\cdot}91$ per cent.).

Tetrabromoresorcinolcoumarein was prepared by heating 3·6 grams of resorcinolcoumarein and 3·2 grams of bromine in glacial acetic acid on a water-bath for one hour, allowing to cool, filtering into a large excess of water, and washing the red precipitate obtained with hot water. The powder, pale red when dry, is soluble in alkalis, alcohol, or ether, but shows no fluorescence in any of these solvents. It decomposes above 280° (Found: $Br = 48{\cdot}83$. $C_{21}H_{12}O_5Br_4$ requires $C = 48{\cdot}18$ per cent.).

In conclusion, I desire to express my thanks to Dr. F. G. Pope for his helpful suggestions and to the Research Fund Committee of the Chemical Society for the grant which defrayed part of the expenses incurred in this research.

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CLXV.—*The Nitro- and Amino-derivatives of* m-*Hydroxybenzoic Acid.*

By Victor Froelicher and Julius Berend Cohen.

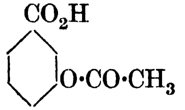
Although Griess and Hübner obtained a *p*-nitro-derivative of *m*-hydroxybenzoic acid in 1872 by the action of potassium hydroxide on 4-nitro-3-aminobenzoic acid (*Ber.*, 1872, **5**, 856), the formation of nitro-derivatives of this acid by direct nitration was first effected by Griess in 1887 (*Ber.*, 1887, **20**, 405) by using dilute nitric acid· He states that he succeeded in obtaining in this way the 2-, 4-, and 5-nitro-*m*-hydroxybenzoic acids.

An attempt to repeat his experiments, according to his directions and by various modifications of them, was unsuccessful. About 20 per cent. of the theoretical amount of the 4-nitro-acid was obtained and at the same time very small quantities of the impure 5- and 6-nitro-acids, but no 2-nitro-acid was found. Although the 6-acid was not isolated in a state of purity, there is no doubt as to its presence, seeing that the 6-amino-acid has been separated from the mixed nitro-acids after reduction.

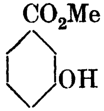
The disadvantage of Griess's method arises from the resinous nature of the product and the consequent difficulty of separating the different isomerides by crystallisation.

Further attempts to separate the acids by crystallisation of the copper, magnesium, and calcium salts met with no better success. Following a suggestion of Dr. J. B. Oesch, nitration was tried in nitrobenzene solution with fuming nitric acid. Although the product was freer from resinous matter, the 2- and 5-acids could not be isolated.

Experiments were then carried out with the following derivatives of *m*-hydroxybenzoic acid :



(I.)



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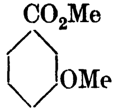

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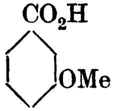
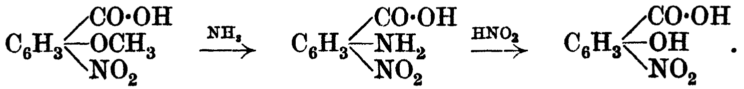


(IV.)

It is an interesting fact that these are all less easily nitrated than the unsubstituted hydroxy-acid, but neither the method of Griess nor that of Oesch is applicable. The acetoxy-derivative (I) cannot be nitrated at all, even on boiling with fuming nitric acid. In presence of concentrated sulphuric acid, however, a vigorous action occurs owing to the hydrolysis of the acetoxyl group, when the free hydroxy-acid is readily attacked. The methyl ester (II) may be nitrated in a solution of carbon tetrachloride with fuming nitric acid at a temperature not exceeding 45°, but a very poor yield of mixed nitro-acids was obtained. The third or methoxy-ester (III) is an oil and was found more difficult to nitrate than II or IV.

The most satisfactory results were obtained with methoxy-benzoic acid (IV), in which nitration was carried out with a mixture of nitric and sulphuric acids in acetic anhydride. In this way the 2- and 4-nitro-acids were formed. They proved to be identical with the substances obtained by Rieche (*Ber.*, 1889, **22**, 2355) by the nitration of methoxybenzaldehyde and subsequent oxidation. He determined the constitution of both acids by transforming them into Griess's acids in the following way :



$$C_6H_3\begin{cases}CO{\cdot}OH\\OCH_3\\NO_2\end{cases} \xrightarrow{NH_3} C_6H_3\begin{cases}CO{\cdot}OH\\NH_2\\NO_2\end{cases} \xrightarrow{HNO_2} C_6H_3\begin{cases}CO{\cdot}OH\\OH\\NO_2\end{cases}.$$

The position of the nitro-group is a matter of some interest. According to Holleman, the position taken by the entrant group is mainly determined by the nature of those already present and to a smaller extent by that of the entrant group itself, and he lays down the following rules (Die Einführung von Substituenten in den Benzolkern):

1. The rate of substitution takes place more rapidly in the ortho- and para- than in the meta-position.

2. The order of influence of groups determining the ortho-para-position taken by the entrant group is:

$$OH > NH_2 > Cl > I > Br > CH_3.$$

3. The order of influence of groups determining the meta-position is:

$$CO_2H > SO_3H > NO_2.$$

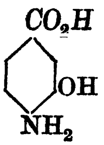
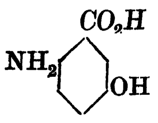
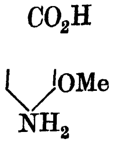
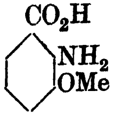
According to this view the entrant nitro-group in *m*-hydroxybenzoic acid should take up the 2-, 4-, or 6-position and to a smaller extent position 5.

In the nitration of the hydroxybenzoic acid the main product is the 4-nitro-compound, whereas in the case of the methoxy-derivative the 2- and 4-nitro-acids both *ortho* to the hydroxyl group are obtained. The methoxyl group differs, therefore, to some extent from the hydroxyl group in its directing influence. Incidentally experiments were made to combine toluenesulphonyl chloride and carbonyl chloride with the sodium or silver salt of hydroxybenzoic acid, but without result.

Reduction of the Nitrobenzoic Acids.

Although, as already stated, the 2-, 4-, and 5-nitro-acids were obtained by Griess, only the 4-nitro-acid has been reduced to the amino-compound (Einhorn, *Annalen*, 1900, **311**, 43; Friedländer, 1901, p. 819, D.R.-P. 97335). The 2-amino-acid was obtained by Keller (*Arch. Pharm.*, 1908, **246**, 21) by heating damascenine with hydriodic acid at 100°. An amino-acid of unknown constitution has been prepared by the "Ciba" Co. of Basle (Friedländer, II, 139, 915) by heating *m*-aminophenol for twelve hours with a solution of ammonium carbonate at 110°. The 6-amino-acid was obtained by Griess (*Ber.*, 1878, **11**, 1733) by heating 6-nitro-*m*-aminobenzoic acid with potassium hydroxide.

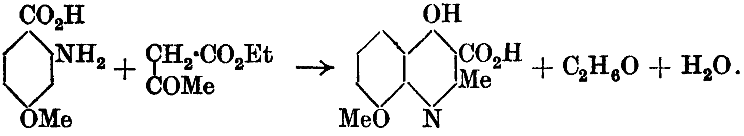
By using Einhorn's method of reduction, the following amino-compounds have been prepared:

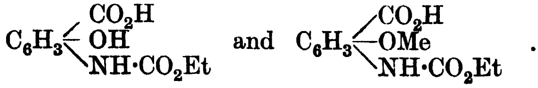
They are typical amino-compounds, forming acetyl and benzoyl derivatives, they react with potassium cyanate, giving carbamido-compounds, and where the amino-group is *ortho* to the carboxyl, hydantoin derivatives. They react with chlorocarbonic ester and are readily diazotised.

The constitution of the 4- and 6-amino-acid has been ascertained as follows. The 4-carbamido-compound loses ammonia when heated near to the melting point (306°), forming an anhydride. It also gives on methylation a product identical with that obtained from the 4-aminomethoxy-acid by the action of potassium cyanate. Both the 2-aminomethoxy-compound and the 6-aminohydroxy-acid yield carbamido-derivatives which readily pass into the hydantoins on heating with hydrochloric acid, thus fixing the *ortho*-position of the amino-group to carboxyl.

Furthermore, the 2-amino-acid reacts with acetoacetic ester, yielding a quinaldine derivative (Niementowski, *Ber.*, 1894, **27**, 1398).



With chlorocarbonic ester all react, giving carbethoxyamino-compounds of the formula



$$C_6H_3\begin{cases}CO_2H\\OH\\NH\cdot CO_2Et\end{cases} \text{ and } C_6H_3\begin{cases}CO_2H\\OMe\\NH\cdot CO_2Et\end{cases}.$$

EXPERIMENTAL.

Nitration of m-*Hydroxybenzoic Acid.*

Fifty grams of the *m*-hydroxy-acid were dissolved in 175 c.c. of hot nitrobenzene. By rapidly cooling, the acid separated in a finely divided state. To the mixture warmed at 35—40°, 17 c.c. of fuming nitric acid dissolved in an equal amount of nitrobenzene were slowly added and stirred for four hours. The product was filtered, washed with carbon tetrachloride, and crystallised from dilute alcohol. It melted at 227—228° and was therefore the 4-nitro-acid. The yield was 10 grams. From the mother-liquor the addition of carbon tetrachloride precipitated a red oil which soon solidified and melted indefinitely at 80—110°. A small quantity of the 6-amino-acid was, however, obtained on reduction, which indicates that some 6-nitro-acid was formed.

Nitration of m-*Methoxybenzoic Acid.*

Fifty grams of *m*-methoxybenzoic acid (Graebe, *Annalen*, 1905, **340**, 211) were added to 400 c.c. of acetic anhydride and cooled in a freezing mixture. A mixture of equal volumes of fuming nitric acid (24 grams) and concentrated sulphuric acid was slowly introduced, the temperature being maintained at – 5° to – 10° and the mixture well stirred. The reaction required about eight hours for completion. The product was allowed to stand overnight and then poured on to ice, filtered, washed with water, and dried. The yield was 50 grams of mixed nitro-acids, which melted, but not sharply, at about 200°. The acids may be separated by repeated fractional crystallisation from water, alcohol, or more conveniently from glacial acetic acid. In this way two pure substances were obtained, the main product being the 4-nitro-acid, with smaller quantities of the 2-nitro-acid, the former melting at 208—211° and the latter at 253—255°. Rieche (*loc. cit.*) gives 208° and 251° (Found: for 4-nitro-acid, $N = 6{\cdot}98$, $7{\cdot}28$; for 2-nitro-acid, $N = 7{\cdot}15$, $7{\cdot}20$. Calc., $N = 7{\cdot}10$ per cent.).

Both compounds are insoluble in benzene, ether, or chloroform. The sodium salt is almost colourless in solution, but becomes yellow on standing.

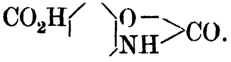
Reduction of the Nitro-acids.

4-*Amino*-m-*hydroxybenzoic Acid.*—The reduction was effected according to Einhorn (*Annalen*, 1900, **311**, 43; Friedländer, 1901, p. 819). Ten grams of the nitro-acid and 200 c.c. of concentrated hydrochloric acid were heated on the water-bath and 30 grams of tin slowly added. After the reaction was complete, the product was allowed to stand for an hour, when the double tin salt separated and was filtered. The precipitate was dissolved in 200 c.c. of warm water and hydrogen sulphide passed in until all the tin was removed. The filtrate was concentrated on the water-bath until crystals of the hydrochloride began to separate. When cold, the hydrochloride was filtered, dissolved in a little water, and the free base precipitated by the addition of a concentrated solution of sodium acetate. The base was filtered and washed with water. It may be recrystallised from hot water or dilute alcohol and melts at 115—116°. The yield is about 60 per cent. of the theoretical.

The hydrochloride, which dissolves readily in water, can be diazotised, giving a yellow, crystalline diazonium salt, which, when dry, explodes on heating and in alkaline solution forms a red colouring matter with resorcinol and β-naphthol.

4-*Carbamido*-m-*hydroxybenzoic Acid.*—Five grams of the amino-acid were added to a solution of 2·5 grams of potassium cyanate in 10 c.c. of water. The reaction was completed by gently warming. The precipitate was removed by filtration and washed with water. When recrystallised from hot water, it melted at 308°, partly decomposing with evolution of ammonia. It dissolved in hot alcohol, but was insoluble in ether, light petroleum, or benzene (Found : N = 14·18. $C_8H_8O_4N_2$ requires N = 14·29 per cent.).

4-*Carbethoxyamino*-m-*hydroxybenzoic Acid.*—Four grams of the amino-acid were dissolved in 150 c.c. of 10 per cent. potassium carbonate solution; 16 grams of ethyl chloroformate were added and the mixture was shaken. The flesh-coloured precipitate formed was filtered, washed with cold water, and purified by dissolving in alcohol and reprecipitating with water. The compound crystallises in colourless leaflets melting at 250—251° and is soluble in water or alcohol, but insoluble in hydrocarbons (Found : N = 6·00. $C_{10}H_{11}O_5N$ requires N = 6·22 per cent.). When slowly heated, it does not melt, but slowly decomposes at 305—310°, forming a dark brown substance which sublimes at about 320°. The same compound may be prepared by dissolving the carbethoxy-compound in sodium hydroxide, warming for an hour on the water-bath, and acidifying with hydrochloric acid. It has probably the following formula :



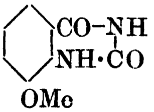
4-*Amino*-m-*methoxybenzoic Acid.*—The reduction of the corresponding nitro-compound was carried out as described above. The amino-acid is a colourless substance which crystallises from hot water in leaflets and melts at 185—186°. It is soluble in alcohol, but insoluble in cold water, light petroleum, or benzene (Found : N = 8·40. $C_8H_9O_3N$ requires N = 8·38 per cent.). The hydrochloride is not very soluble in water, and is hydrolysed in the hot solution. The acetyl derivative is a colourless, crystalline compound which melts at 217°. As it is readily hydrolysed by dilute sulphuric acid (1 : 1) on the water-bath, the conversion of the base into the acetyl derivative may be used as a means of purification.

4-*Carbamido*-m-*methoxybenzoic Acid.*—0·5 Gram of the amino-acid was added to a solution containing 0·25 gram of potassium cyanate. After warming, the carbamido-compound was precipitated in the cold by hydrochloric acid. It was filtered and recrystallised from hot alcohol or acetic acid and melted at 228° (Found: N = 13·38. $C_9H_{10}O_4N_2$ requires N = 13·34 per cent.).

4-*Carbethoxyamino*-m-*methoxybenzoic Acid.*—This compound was prepared in the manner already described. It melts at 201—203° and is soluble in hot alcohol, from which it may be recrystallised (Found: N = 6·00. $C_{11}H_{13}O_5N$ requires N = 5·85 per cent.).

2-*Amino*-m-*methoxybenzoic acid* was prepared by the same method as that already described. It is less soluble in alcohol or water than the 4-amino-acid, but is readily crystallised from acetic acid, forming slightly brown leaflets which melt at 170—171° (Found: N = 8·39. $C_8H_9O_3N$ requires N = 8·38 per cent.). The hydrochloride is hydrolysed by cold water. The acetyl derivative crystallises in colourless needles, m. p. 208°.

2-*Carbamido*-m-*methoxybenzoic acid* was prepared in the manner already described and crystallises in leaflets, m. p. 160° (Found: N = 13·46. $C_9H_{10}O_4N_2$ requires N = 13·34 per cent.). It is soluble in hot water or alcohol, and insoluble in cold water, ether, or benzene. On boiling with hydrochloric acid, a white precipitate is formed which, after being washed with cold water and twice crystallised from hot water, melts at 258—259° and is the hydantoin of the formula:



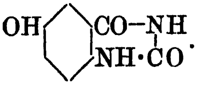
(Found: N = 14·65. $C_9H_8O_3N_2$ requires N = 14·58 per cent.). It is insoluble in ether or benzene and is very soluble in hot alcohol.

2-*Carbethoxyamino*-m-*methoxybenzoic acid* was prepared by the method already described. It melts at 152—154° and crystallises in white leaflets (Found: N = 5·96. $C_{11}H_{13}O_5N_2$ requires N = 5·85 per cent.). It may be purified by dissolving in alcohol and precipitating with water. It is very soluble in alcohol and is insoluble in ether, benzene, or light petroleum.

Methoxy-γ-hydroxyquinaldine-β-carboxylic Acid.—On boiling the 2-amino-acid with an excess of acetoacetic ester for two to three hours, a yellow, crystalline compound separates, when, in order to avoid the formation of resinous by-products, the reaction is stopped. The mixture is filtered and washed with water. The substance melts at 270°.

6-*Amino*-m-*hydroxybenzoic Acid.*—When *m*-hydroxybenzoic acid was nitrated, a mixture of nitro-compounds was obtained which could not be separated; but on reduction a pure amino-compound, m. p. 233—234°, was isolated.

6-*Carbamido*-m-*hydroxybenzoic acid* was prepared by the method already described. It crystallises from acetic acid in small prisms, and melts and decomposes at 166—167° (Found: N = 14·12. $C_8H_8O_4N_2$ requires N = 14·29 per cent.). It is slightly soluble in hot alcohol or hot water, but is insoluble in ether or benzene. On boiling with hydrochloric acid, it is converted into the hydantoin, which does not melt but sublimes above 360° (Found: N = 15·80. $C_8H_6O_3N_2$ requires N = 15·73 per cent.). It has the formula



We gratefully acknowledge the interest which Dr. J. B. Oesch has taken in the research.

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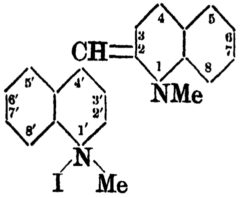
CLXVI.—*A Comparison of some Isomeric* iso*Cyanines.*

By FRANCES MARY HAMER.

IN this paper, the preparation of certain isomeric *iso*cyanines is described. The work was undertaken with the object of comparing the photographic sensitising action of a series of isomerides, in order to determine the effect produced by a given substituent when introduced into various positions in the molecule. The absorption spectra of the sixteen *iso*cyanines were also photographed, for comparison with the spectrographs illustrating the sensitisation. That a connexion exists between sensitising and absorption bands has long been known; in the *iso*cyanine group the subject was studied by Sheppard in the case of four dyes (*B. J. Ph.*, 1908, **55**, 679) and it seemed desirable to investigate how far the relationship is a general one.

In the following formula (Mills and Wishart, T., 1920, **117**, 579) the numerals indicate the system of nomenclature:



This substance, 1 : 1′-dimethyl*iso*cyanine iodide, is obtained by the action of alcoholic sodium hydroxide on a solution of quinoline methiodide and quinaldine methiodide; it was desired to prepare a series of its derivatives in which the same substituent should occupy the 5, 6, 7, 8, 5′, 6′, 7′, and 8′ positions respectively, which object should be attainable through the condensation of quinoline methiodide with each of the suitably substituted quinaldine methiodides and of quinaldine methiodide with each of the appropriate quinoline methiodides. On account of the readiness with which it can be introduced into various positions in the quinoline and quinaldine nuclei, the nitro-group was at first selected. Here an unforeseen difficulty arose, since in the three different preparations that were attempted *iso*cyanine formation did not occur, presumably owing to the presence of the nitro-group, although this is contrary to an observation of Decker and Remfry (*Ber.*, 1905, **38**, 2773). By reduction of the nitro-quinolines and -quinaldines, followed by acetylation, the corresponding acetylamino-derivatives resulted, and the methiodides of these bases were utilised for making the acetylamino-1 : 1′-dimethyl*iso*cyanine iodides. By hydrolysis of these dyes, *iso*cyanines containing an amino-group were prepared, although they could not be obtained directly by condensation of two methiodides. In the third series, isomerism is due to the varying positions of the cinnamoylamino-group, which was chosen because of the possibility that its unsaturated character would influence the sensitisation.

The acetylamino-, amino-, and cinnamoylamino-groups were actually introduced into the 5, 6, 7, 6′, and 7′ positions in the *iso*cyanine molecule, but it appeared that a 5-substituted quinoline methiodide cannot give rise to a compound of this type. Thus neither 5-acetylaminoquinoline methiodide nor 5-cinnamoylaminoquinoline methiodide reacts with quinaldine methiodide to form an *iso*cyanine. This fact is of interest as confirming the formula of Mills and Wishart (*loc. cit.*), in which the quinoline residue is linked through the 4′ position to the quinaldine nucleus, since with a linking of this kind the production of a 5′-substituted *iso*cyanine would be opposed by steric hindrance. A low yield of dye was obtained in two instances from quinaldine methiodide and a 7-substituted quinoline methiodide, although it is not apparent why a substituent thus situated should inhibit the condensation. Steric hindrance comes into play in preventing the formation of the methiodides of 8-acetylaminoquinoline and of 8-acetylaminoquinaldine, and no *iso*cyanines were prepared containing a substituent in the 8 or 8′ positions.

The photographs of the sensitising bands show that, when a cinnamoylamino-group is introduced into the molecule of 1 : 1′-dimethyl*iso*cyanine iodide, it exerts a considerable depressant effect, except in the instance where it occupies the 6 position, for 6-cinnamoylamino-1 : 1′-dimethyl*iso*cyanine iodide is a powerful sensitiser and the band in the red is particularly intense. With the spectrographs of the other members of the series both crests are approximately equal in height and the sensitising action is very low, falling to a minimum in the case of 5-cinnamoylamino-1 : 1′-dimethyl*iso*cyanine iodide. In the acetylamino-series the 6′-derivative is distinctly the best sensitiser and is not inferior to the parent substance in this respect; the substituent does, however, reveal a tendency to depress the sensitisation and this effect is most potent in the case of 5-acetylamino-1 : 1′-dimethyl*iso*cyanine iodide. The amino-group, on the contrary, invariably enhances the sensitising action, and the amino-1 : 1′-dimethyl*iso*cyanine iodides are very powerful sensitisers, the spectrographs of which are all similar and show a uniform band. From the three series it is evident that the magnitude of the influence on the sensitising action exerted by a given substituent varies largely according to the situation of this group. It may be noted that, when it is the hydrogen in the 5 position that has been replaced, the extension of the sensitising band into the red is at a minimum. Apart from this, no conclusions of a general character can be drawn as to the effect of introducing a given substituent into a particular position in the molecule.

The sensitising and absorption spectra correspond in possessing two bands, of which the one nearer the red appears to afford a better basis of comparison than does that in the more refrangible region, first, because its variations in position are of greater magnitude, and secondly, because with some of the absorption photographs this band is distinctly larger and more clearly defined than is the other, and is presumably of greater importance. By plotting the positions of these maxima in the acetylamino-, cinnamoylamino-, and amino-series for both sensitisation and absorption, certain relationships were brought out.

1 : 1′-Dimethyl*iso*cyanine iodide was compared with its derivatives with regard to the position of the α-band in the absorption spectrographs, whilst a similar comparison was made with the photographs showing the sensitisation. From this it appears that in two instances this band in the parent substance is nearer to the red than is that in the derivative of higher molecular weight, and in five cases they coincide, whilst the remaining twenty-two conform to Nietzki's rule, that an increase in molecular weight causes a shift of the bands towards the red.

With each of these *iso*cyanines the α-sensitising maximum is situated 200—350 tenth metres nearer the red end of the spectrum than is the corresponding absorption band. In the sensitising curves of the three series studied it is found that, without exception, this crest in the cases of the 6, 7, and 6′-substituted *iso*cyanines lies nearer to the red than does that in the equivalent 5- and 7′-substituted dyes. There is correlation between the sensitising and absorption spectra in that an identical relationship holds in the latter case.

EXPERIMENTAL.

6-*Nitroquinaldine.*—This compound has been prepared by condensation of 3-nitro-6-aminobenzaldehyde with acetone (Cohn and Springer, *Monatsh.*, 1903, **24**, 87) and is described as melting at 173—174°. In the present work it was obtained by the reaction of *p*-nitroaniline, an equal weight of hydrochloric acid, and 25 per cent. excess of the theoretical quantity of paraldehyde. The mixture was heated on a water-bath for half an hour, poured into twice its volume of water, and filtered to remove tar. The 6-nitroquinaldine was precipitated by addition of sodium acetate, and was purified through its nitrate. On recrystallisation, the melting point became constant at 164°.

6-*Nitroquinaldine Methiodide.*—The methiodide could not be prepared by heating 6-nitroquinaldine with methyl iodide, but was obtained by employing methyl sulphate. It forms green crystals, which are readily soluble both in alcohol and water, and melts with decomposition at 214° (Found: I = 38·50. $C_{11}H_{11}O_2N_2I$ requires I = 38·46 per cent.).

6-*Nitroquinoline Methiodide.*—The large orange crystals of this salt are very soluble in water and less so in alcohol. Decomposition begins at about 230°, followed by melting at about 245° (Found: I = 40·27. $C_{10}H_9O_2N_2I$ requires I = 40·17 per cent.).

Amino-quinolines and -quinaldines.

5-*Aminoquinaldine.*—Crystals of 5-aminoquinaldine are said to lose water at 100°, leaving the anhydrous base which melts at 104—105° (Doebner and v. Miller, *Ber.*, 1884, **17**, 1698). It was, however, found that the brown anhydrous substance, which was obtained by drying the yellow crystals at 105° and in a vacuum desiccator, melted at 117—118°.

6-*Aminoquinaldine.*—This compound was prepared by reduction of 6-nitroquinaldine with stannous chloride and hydrochloric acid, treatment with sodium hydroxide, filtration, and extraction of the solid with hot alcohol. It is moderately soluble in hot water, but almost insoluble in cold, from which it comes down as small pale brown crystals; it is very soluble in chloroform and rectified spirit and can be recrystallised from dilute alcohol. The melting point is 187·5° (Found: N = 17·56. $C_{10}H_{10}N_2$ requires N = 17·72 per cent.).

7-*Aminoquinoline*.—It has been stated by Claus and Massau (*J. pr. Chem.*, 1893, [ii], **48**, 170) that 7-aminoquinoline melts at 188°, but this was not found to be the case. As prepared by reduction of 7-nitroquinoline, the amino-compound was obtained as a yellow solid melting at 73·5° and containing water of crystallisation, whilst the anhydrous base melted sharply at 93·5—94° (Found: N = 18·92. $C_9H_8N_2$ requires N = 19·44 per cent.).

It is noteworthy that solutions of 7-aminoquinoline and 7-aminoquinaldine, and their salts, exhibit powerful fluorescence, and that with both the 6-derivatives the effect is considerably smaller, whilst in the case of the 5- and 8-aminoquinolines and of the 5- and 8-aminoquinaldines no fluorescence is shown.

Cinnamoylamino-quinolines and -quinaldines and their Methiodides.

To prepare a cinnamoylamino-quinoline or -quinaldine the corresponding amino-compound was dissolved in chloroform, and while being kept cool was treated with the theoretical amount of cinnamoyl chloride, also in chloroform solution, when heat was evolved and generally a red or yellow substance crystallised. The mixture was shaken with the calculated quantity of *N*-sodium hydroxide until almost colourless, and the cinnamoylamino-derivative was filtered off and recrystallised from rectified spirit, when the yield of pure product was about 72 per cent. of the theoretical. 7-Cinnamoylaminoquinoline differs from the other cinnamoylamino-compounds in being readily soluble in chloroform, and in this instance the yield was low owing to difficulties in effecting the purification. All the bases are moderately soluble in spirit and insoluble in water; they are pale yellow.

The methiodides were all prepared in the same way, namely, by heating the cinnamoylamino-quinoline or -quinaldine and 10 per cent. excess of methyl iodide, sometimes with the addition of chloroform, in a sealed tube at 100° for twenty-four to forty-eight hours. The resulting salts were recrystallised from alcohol or water, and the yield of pure product was usually 80—90 per cent. of the theoretical quantity. On heating the methiodides, decomposition occurred both before and after melting, and the melting points recorded are not definite, but depend on the rate of rise of temperature.

5-*Cinnamoylaminoquinaldine* crystallises as beautiful, highly refractive, pale yellow prisms, and melts at 257° (Found: N = 9·71. $C_{19}H_{16}ON_2$ requires N = 9·72 per cent.).

5-*Cinnamoylaminoquinaldine Methiodide*.—In the preparation of this salt the yield was only 51 per cent. and the rest of the base was recovered unchanged. The methiodide is easily soluble both in alcohol and in water and forms minute yellow crystals, which turn orange on becoming anhydrous. The melting point is 228—234° (Found: I = 29·28. $C_{20}H_{19}ON_2I$ requires I = 29·51 per cent.).

6-*Cinnamoylaminoquinaldine* forms almost colourless crystals melting at 256·5° (Found: N = 9·51. $C_{19}H_{16}ON_2$ requires N = 9·72 per cent.).

6-*Cinnamoylaminoquinaldine methiodide* crystallises in fine yellow needles, which on heating begin to decompose at 247° and melt at about 269° (Found: I = 29·50. $C_{20}H_{19}ON_2I$ requires I = 29·51 per cent.).

7-*Cinnamoylaminoquinaldine* formed yellow crystals which melted at 128·5—129·5°; after a second recrystallisation the substance became sticky at 128°, but did not melt until 223°, although it melted if left in the steam-oven for some time. A nitrogen estimation was made on the base which had been recrystallised once and melted at 128·5—129·5° (Found: N = 9·35. $C_{19}H_{16}ON_2$ requires N = 9·72 per cent.).

7-*Cinnamoylaminoquinaldine Methiodide*.—In this preparation it is important to avoid a large excess of methyl iodide. The methiodide is yellow and is moderately soluble in dilute alcohol. Decomposition starts at 260° and the melting point is about 280° (Found: I = 29·02. $C_{20}H_{19}ON_2I$ requires I = 29·51 per cent.).

5-*Cinnamoylaminoquinoline* forms small, yellow crystals of melting point 259° (Found: N = 10·10. $C_{18}H_{14}ON_2$ requires N = 10·22 per cent.).

5-*Cinnamoylaminoquinoline methiodide* is a yellow substance readily soluble in hot water. It melts at about 238° (Found: I = 30·49. $C_{19}H_{17}ON_2I$ requires I = 30·50 per cent.).

6-*Cinnamoylaminoquinoline* forms white crystals which are very soluble in alcohol. When the substance was very slowly heated, it became sticky at 170°, yellower and more sticky at about 184°, and melted sharply at 199°; if, however, the temperature was raised somewhat more rapidly, the compound melted at 184° to a pale yellow fluid, which, when gradually heated, crystallised again, and the yellow crystals produced melted at 199°, giving a darker liquid. It may be that the melting points 184° and 199° correspond with isomeric *cis*- and *trans*-forms of the base, and it would seem that above 184° the form of lower m. p. undergoes conversion into that of higher m. p.; similar anomalies with regard to melting point were observed in the case of 7-cinnamoylaminoquinaldine (Found : N = 10·23. $C_{18}H_{14}ON_2$ requires N = 10·22 per cent.).

6-*Cinnamoylaminoquinoline methiodide* gives yellow crystals which become orange in the steam-oven. At 110°, the yellow substance began to turn orange, and at 150° was as deep in colour as the other crystals, but on raising the temperature to 170° both specimens became yellow. At 249° decomposition commenced and the salt melted at about 274° (Found : I = 30·53. $C_{19}H_{17}ON_2I$ requires I = 30·50 per cent.).

7-*Cinnamoylaminoquinoline* is white when pure and melts at 202° (Found: N = 10·15. $C_{18}H_{14}ON_2$ requires N = 10·22 per cent.).

7-*Cinnamoylaminoquinoline methiodide* crystallises as yellow needles which melt at 280° with much decomposition (Found : I = 30·72. $C_{19}H_{17}ON_2I$ requires I = 30·50 per cent.).

Acetylamino-quinolines and -quinaldines and their Methiodides.

The amino-quinoline or -quinaldine was added to twice the calculated quantity of acetic anhydride and the mixture was heated in a water-bath for fifteen minutes, after which the product was cooled, diluted with water, and treated with excess of ammonia to precipitate the required acetylamino-derivative. On recrystallisation from water or alcohol, all these compounds formed white crystals, which became anhydrous on drying in the steam-oven.

Methiodides were prepared by the action of methyl iodide on the acetylamino-derivatives and, except in the instance of 7-acetylaminoquinaldine methiodide, the yield of pure product was 80—90 per cent. of the theoretical. With 8-acetylaminoquinoline and 8-acetylaminoquinaldine, steric hindrance came into play, so that their methiodides could not be obtained either by the action of methyl iodide on the base or by employing methyl sulphate.

5-*Acetylaminoquinaldine* has m. p. 204·5° (Found : N = 13·91. $C_{12}H_{12}ON_2$ requires N = 14·01 per cent.).

5-*Acetylaminoquinaldine Methiodide*.—The orange crystals are very soluble in water and moderately so in alcohol. Decomposition begins at about 244° and the melting point is 250—260° (Found : I = 37·05. $C_{13}H_{15}ON_2I$ requires I = 37·11 per cent.).

6-*Acetylaminoquinaldine* has m. p. 168·5° (Found : N = 14·13. $C_{12}H_{12}ON_2$ requires N = 14·01 per cent.).

6-*Acetylaminoquinaldine methiodide* forms pale yellow crystals which begin to decompose at about 254° (Found : I = 37·31. $C_{13}H_{15}ON_2I$ requires I = 37·11 per cent.).

7-*Acetylaminoquinaldine* has m. p. 194° (Found : N = 13·93. $C_{12}H_{12}ON_2$ requires N = 14·01 per cent.).

7-*Acetylaminoquinaldine methiodide* is very soluble in alcohol or hot water, and slightly soluble in cold water; the colour of the crystals is orange or yellow. Decomposition starts at 240° and the melting point is about 267° (Found : I = 36·99. $C_{13}H_{15}ON_2I$ requires I = 37·11 per cent.).

5-*Acetylaminoquinoline methiodide* is a bright yellow substance which is very soluble in water. When heated, it darkens at 255° and melts at 260—264° (Found : I = 38·64. $C_{12}H_{13}ON_2I$ requires I = 38·69 per cent.).

6-*Acetylaminoquinoline methiodide* separates from hot water as beautiful yellow crystals. Darkening begins at 270° and the melting point is 317° (Found : I = 38·50. $C_{12}H_{13}ON_2I$ requires I = 38·69 per cent.).

7-*Acetylaminoquinoline* has m. p. 167·5° (Found : N = 15·02. $C_{11}H_{10}ON_2$ requires N = 15·06 per cent.).

7-*Acetylaminoquinoline methiodide* crystallises in yellow prisms, which darken at 267°, are black at 300°, and melt at 295—310° (Found : I = 38·79. $C_{12}H_{13}ON_2I$ requires I = 38·69 per cent.).

1 : 1′-*Dimethyl*isocyanine *Iodide.*

5·78 Grams of quinoline methiodide (2 mols.) and 2·85 grams of quinaldine methiodide (1 mol.) were dissolved in 100 c.c. of boiling rectified spirit, into which was poured a hot solution of 0·27 gram of sodium (1·2 mols.) in 30 c.c. of alcohol. After gentle boiling for fifteen minutes, the mixture was treated with 1 c.c. of acetic acid and was left overnight before being filtered. 1 : 1′-Dimethyl-*iso*cyanine iodide, after recrystallisation from methyl alcohol, was obtained as beautiful, lustrous green needles, which melted with decomposition at 268° (Found : I = 29·62. $C_{21}H_{19}N_2I$ requires I = 29·81 per cent.).

The substance is a powerful sensitiser. For moderate exposures the sensitisation extends to 6500, and there are two maxima at 5850 and 5350. The crests of the absorption bands lie at 5550 and 5200.

Attempts to Prepare Nitro-1 : 1′-*dimethyl*isocyanine *Iodides.*

The presence of a nitro-group in the quinoline or quinaldine nucleus appears to prevent *iso*cyanine formation. Thus 6-nitroquinoline methiodide does not condense with quinaldine methiodide to yield a compound of this type, neither does quinoline methiodide give an *iso*cyanine with 5-nitroquinaldine methiodide or 6-nitroquinaldine methiodide.

The Cinnamoylamino-1 : 1′-*dimethyl*isocyanine *Iodides.*

By condensation of each cinnamoylaminoquinoline methiodide with quinaldine methiodide, and of the cinnamoylaminoquinaldine methiodides with quinoline methiodide, the preparation of six *iso*cyanines was attempted. The quantities taken and the method of preparation were analogous with what has been described in the case of the parent substance. When one of the mixed methiodides was insufficiently soluble in rectified spirit, this solvent was diluted with water.

5-*Cinnamoylamino*-1 : 1′-*dimethyl*isocyanine *Iodide*.—The dye forms minute, purple crystals, which on being crushed show a green, metallic lustre. Decomposition proceeds rapidly from 185° and melting occurs at about 200—230°.

This substance is the feeblest sensitiser which was prepared. For moderate exposures the sensitisation extends to 6100, and there is a crest at 5850 and another weaker one at 5450. When a very long exposure is given, there is an extension to 6850 and another band appears, with its maximum at 6500. The absorption maxima lie at 5600 and 5250.

6-*Cinnamoylamino*-1 : 1′-*dimethyl*isocyanine *Iodide*.—This substance forms compact, purple crystals with a golden lustre. On heating, decomposition is rapid from 270° and the melting point is at about 280—284°. For analysis, crystals were dried in a vacuum at 112° until the weight was constant and the iodine was estimated by the method of Carius (Found : I = 21·85. $C_{30}H_{26}ON_3I$ requires I = 22·22 per cent.).

The *iso*cyanine gives very clean plates and is by far the most powerful sensitiser of the cinnamoylamino-group. The band reaches to 6500 and there is a maximum at 6000, which is more intense than that in the green at 5500. The absorption crests lie at 5750 and 5350.

7-*Cinnamoylamino*-1 : 1′-*dimethyl*isocyanine *iodide* forms minute purple crystals which exhibit a brassy lustre. The compound melts with decomposition at about 280°. An iodine estimation was made by Carius's method (Found: I = 21·99. $C_{30}H_{26}ON_3I$ requires I = 22·22 per cent.).

The substance is a weak sensitiser, although better than 5-cinnamoylamino-1 : 1′-dimethyl*iso*cyanine iodide. For moderate exposures the sensitisation extends to 6200 and there are two bands with crests at 5950 and 5400 respectively. The absorption spectrum was not photographed.

*Attempt to Prepare 5′-Cinnamoylamino-*1 : 1′-*dimethyl*iso*cyanine Iodide.*—Quinaldine methiodide and 5-cinnamoylaminoquinoline methiodide react in the presence of alkali to give red compounds, but no *iso*cyanine is produced.

6′-*Cinnamoylamino*-1 : 1′-*dimethyl*iso*cyanine Iodide.*—This is a reddish-purple substance with a brassy iridescence. When heated, it begins to decompose at about 210° and melts at about 247°.

The limit of sensitisation is at 6300 and the faint bands have their crests at 5950 and 5450. The maxima of the absorption curves lie at 5700 and 5300.

7′-*Cinnamoylamino*-1 : 1′-*dimethyl*iso*cyanine Iodide.*—The preparation was carried out as in other instances, but the colour of the reaction mixture was red instead of purple, showing that little of the dye had been produced, and the yield of recrystallised product was exceptionally low. The substance forms small crystals of a dull purple colour, and it is more soluble in methyl alcohol than are its isomerides. When put into a bath at 180°, decomposition begins, and melting occurs over a long range in the region of 200°. The compound is a poor sensitiser, like its isomerides, which contain the cinnamoylamino-group in the 7 and 6′ positions respectively. For moderate exposures the sensitisation extends to 6200 with a very faint continuation as far as 6500. The crests are at 5900 and 5400. The maxima of the absorption bands lie at 5600 and 5200.

The Acetylamino-1 : 1′-*dimethyl*iso*cyanine Iodides.*

5-*Acetylamino*-1 : 1′-*dimethyl*iso*cyanine Iodide.*—This dye forms small, brown crystals with a metallic appearance, and it also crystallises as larger, very beautiful needles with a green or steel blue iridescence. When the latter are heated, decomposition begins at about 195°, whilst melting occurs gradually and is complete at temperatures which vary between 240° and 260°, according to the rate of heating.

With the pure *iso*cyanine which had been recrystallised four times, fogging of the photographic plate occurred; this sensitiser is the poorest of the acetylamino-series and is considerably inferior to the parent substance. The spectrograph shows two maxima at 5850 and 5400. The crests of the absorption bands lie at 5600 and 5250.

6-*Acetylamino*-1 : 1′-*dimethyl*iso*cyanine Iodide.*—The substance forms little green crystals, and also larger, less soluble, green and gold prisms which are very beautiful. Compact bronze crystals were also produced, but these different varieties all produce the same spectrograph. Melting occurs at 268° with decomposition (Found: I = 26·00. $C_{23}H_{22}ON_3I$ requires I = 26·27 per cent.).

The spectrograph is similar to that of the isomeric compound derived from quinoline methiodide and 5-acetylaminoquinaldine methiodide, but the plate is not fogged and the sensitisation is stronger. There are two maxima at 5950 and 5300 and the band reaches 6650, whilst in the absorption spectrum the maxima occur at 5700 and 5300.

7-*Acetylamino*-1 : 1′-*dimethyl*iso*cyanine Iodide*.—Minute purple crystals with a brilliant green lustre, and also green crystals, were obtained. When the former are put into a bath at 260° and the temperature is raised, melting with decomposition takes place between 280° and 290°. For analysis, the *iso*cyanine was dried in a vacuum desiccator (Found: I = 25·97. $C_{23}H_{22}ON_3I$ requires I = 26·27 per cent.).

The dye is a good sensitiser, showing a fairly uniform band, which extends to 6650. There is a maximum at 5900 and the second curve is broad with its crest at 5350. The two points of greatest absorption lie at 5650 and 5300.

Attempt to Prepare 5′-*Acetylamino*-1 : 1′-*dimethyl*iso*cyanine Iodide*.—When an alcoholic solution of quinaldine methiodide and 5-acetylaminoquinoline methiodide was acted on with alkali, the colour of the liquid was red instead of purple and the product clearly contained very little *iso*cyanine; by fractional crystallisation from methyl alcohol it was sometimes possible to isolate a minute amount of such a substance. For the sake of comparison, 1 : 1′ : 2′-trimethyl*iso*cyanine iodide was prepared from quinaldine methiodide: (*a*) in appearance the two dyes were indistinguishable; (*b*) on heating three specimens simultaneously, it was observed that 1 : 1′ : 2′-trimethyl*iso*cyanine iodide melted at 282—285°, and the other *iso*cyanine at 275—280°, whilst the mixed melting point was 282—285°; (*c*) the spectrographs were identical as regards the position of the sensitising maxima and the extent of the band, but with the compound prepared from quinaldine methiodide alone the sensitisation was stronger than in the other instance. It was therefore concluded that the substances are identical, and the recognised impurity in the case of that *iso*cyanine in the preparation of which two methiodides were employed seems sufficient to account for the slight variation in the spectrographs and in melting point. Thus 5-acetylaminoquinoline methiodide and quinaldine methiodide do not undergo the *iso*cyanine condensation.

6′-*Acetylamino*-1 : 1′-*dimethyl*iso*cyanine Iodide*.—The smaller crystals of this substance have a purplish-brown colour, but it also forms large, compact crystals with a green, metallic reflex. Melting occurs at about 310° with decomposition. For analysis, the *iso*cyanine was dried in a vacuum desiccator until of constant weight (Found : I = 26·36. $C_{23}H_{22}ON_3I$ requires I = 26·27 per cent.).

The sensitising maxima are at 6000 and 5400; the more powerful sensitisation ceases at 6500, but there is a faint extension to 6900. The most powerful absorption occurs at 5650 and 5300.

*7′-Acetylamino-*1 : 1′*-dimethyl*iso*cyanine Iodide.*—The yield of this *iso*cyanine was remarkably low. The crystals are coloured olive-green with a greenish-yellow lustre and melt with decomposition at about 250—260°. For analysis, the dye was dried at 100° (Found : I = 25·98. $C_{23}H_{22}ON_3I$ requires I = 26·27 per cent).

The sensitising band is almost uniform and for moderate exposures extends to 6600. The crests are at 5850 and 5300, whilst those of the absorption spectra lie at 5550 and 5250.

*The Amino-*1 : 1′*-dimethyl*iso*cyanine Iodides.*

It was found that an *iso*cyanine containing an amino-group could not be produced directly by the condensation of two methiodides, but was obtainable by hydrolysis of the corresponding acetylamino-derivative. This was effected by boiling 0·5 gram of the latter with 7 c c. of concentrated hydrochloric acid for half an hour. The red liquid was cooled and diluted with water and on neutralising it with ammonia the amino*iso*cyanine was precipitated; it was filtered off and recrystallised from methyl alcohol.

These amino-compounds differ from the acetylamino*iso*cyanines in having a considerably greater solubility in methyl alcohol, and by their more strongly marked metallic lustre. They are without exception very powerful sensitisers, showing that the introduction of an amino-group into the molecule of the parent substance enhances the sensitising action.

*5-Amino-*1 : 1′*-dimethyl*iso*cyanine Iodide.*—The small purple crystals show a green lustre, and melt at 250—255° with decomposition. An almost uniform sensitising band extends from the blue to the orange, with a limit for moderate exposures at 6600; there are two maxima at 5850 and 5350. This member of the series exhibits the most intense sensitising action, but with the other four the band extends somewhat further into the red. The crests of the absorption curves lie at 5550 and 5200.

*6-Amino-*1 : 1′*-dimethyl*iso*cyanine Iodide.*—The dye forms compact, dark green crystals and also others of a bright green colour with a golden iridescence. The former begin to decompose at 250° and melt at about 260°, whilst the latter melt at about 266—271°. An iodine estimation was made on a specimen which had been dried in a vacuum desiccator (Found: I = 28·81. $C_{21}H_{20}N_3I$ requires I = 28·77 per cent.).

The sensitisation resembles that of the isomeric substance where the amino-group occupies the 5 position, but it is less intense; it extends rather further into the red, reaching 6700. There are maxima at 6050 and 5400, and the latter band is broader than in the case of the corresponding 5-derivative. The maximum absorption occurs at 5750 and 5350.

7-*Amino*-1 : 1′-*dimethyl*iso*cyanine Iodide*.—Small green crystals, and also prisms with a copper-like appearance, are formed. When the latter are heated, decomposition begins at 225° and the melting point is about 250°.

The limit of sensitisation is reached at 6700 and the crests are at 6050 and 5500. The absorption maxima lie at 5700 and 5350 respectively.

6′-*Amino*-1 : 1′-*dimethyl*iso*cyanine Iodide*.—This *iso*cyanine forms small, green, brilliantly iridescent prisms, m. p. 266—271° after much decomposition. Before analysis the dye was dried in a vacuum desiccator (Found: I = 28·52. $C_{21}H_{20}N_3I$ requires I = 28·77 per cent.).

The band of extra sensitiveness extends to 6700, with maxima at 6000 and 5500. The crests of the absorption curves are at 5700 and 5350.

7′-*Amino*-1 : 1′-*dimethyl*iso*cyanine Iodide*.—The substance was obtained as a purple precipitate, which on boiling with insufficient methyl alcohol for complete solution changed to green and gold pleochroic crystals. Decomposition becomes apparent at 250° and the melting point is fairly constant at 259—260°.

The uniform sensitising band reaches 6600 and the crests occur at 5800 and 5300. The absorption maxima are at 5450 and 5100.

This subject of study was suggested by Dr. W. H. Mills, to whom I am very grateful for his constant help. My thanks are also due to Mr. F. J. Stoakley, who gave invaluable assistance with the photography. I am moreover indebted to the Department of Scientific and Industrial Research for a grant which enabled the work to be carried out.

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CLXVII.—*A New Method for the Preparation of α-Acylphenylhydrazines.*

By Wallace Frank Short.

In the study of another problem it became necessary to prepare certain α-acylphenylhydrazines in quantity. Although up to the present time these substances have been obtained by three methods, none of them can be considered as really satisfactory for their preparation, since all are wasteful and troublesome in application, and use as starting materials substances difficult to prepare and not on the market. These methods may be briefly reviewed in chronological order as follows:

(1) Michaelis and Schmidt (*Ber.*, 1887, **20**, 43, 1713; *Annalen*, 1889, **225**, 300) prepared the α-acyl derivatives of phenylhydrazine by treating its sodio-derivative, suspended in benzene, with acid chlorides or anhydrides. In the preparation of the sodio-derivative, the yield is poor owing to the reduction of a considerable quantity of phenylhydrazine to aniline and ammonia; moreover, the subsequent treatment with acid chloride or anhydride yields both the β-acyl and αβ-diacyl compounds in addition to the substance required.

(2) In 1893, Widman (*Nova. Acta Reg. Soc. Ups.* III, 1893; *Ber.*, 1894, **27**, 2965) found the αβ-diacylphenylhydrazines lose the β-acyl group when boiled with dilute sulphuric acid. The yield of α-acylhydrazine obtained amounts to but 10 per cent. of the diacyl compound employed.

(3) Von Pechmann and Runge (*Ber.*, 1894, **27**, 1698) found that the acylarylformazyl hydrides yield a mixture of hydrazine and hydrazide on reduction with zinc dust and sulphuric acid in presence of alcohol. Thus, acetylphenylformazyl hydride, NAcPh·N:CH·N:NPh, yields *s*-formylphenylhydrazine, CHO·NH·NHPh, and α-acetylphenylhydrazine, $NAcPh·NH_2$.

These methods did not appear to be capable of modifications which would increase the yields to any great extent, and it was therefore decided to obtain a new source for these substances.

At the outset the acylchloroanilides appeared to afford the most desirable starting materials owing to the ease with which they can be prepared (Chattaway and Orton, T., 1899, **75**, 1046, etc.). Hofmann (*Ber.*, 1882, **15**, 407) showed that the aliphatic bromoamides react with ammonia with the production of the amide and the evolution of nitrogen, and it was found that the acylchloroaminobenzenes behave in exactly the same manner. In fact, it was found possible to estimate *N*-chloroacetanilide in a mixture of this substance with acetanilide by passing dry ammonia into a benzene solution and measuring the amount of nitrogen evolved in accordance with the equation

$$3NClPh{\cdot}CO{\cdot}CH_3 + 5NH_3 = 3NHPh{\cdot}CO{\cdot}CH_3 + 3NH_4Cl + N_2.$$

Eventually it was found that by treating a cold benzene solution of the chloroanilides with a suspension of finely divided sodamide in the same solvent, excellent yields of the α-acylhydrazines could be obtained. It is essential for the success of the operation that the sodamide should be quite free from sodium hydroxide and that all the materials should be quite dry. By operating in liquid ammonia instead of benzene, the yields are increased, but not to an extent sufficiently great to compensate for the more elaborate manipulation involved.

It has also been found that diacetylhydrazobenzene may be conveniently prepared by treating *N*-chloroacetanilide with the sodio-derivative of acetanilide in ether.

EXPERIMENTAL.

N-*Chloroacetanilide and Ammonia.*

A current of dry ammonia was passed into a solution of 1·0256 grams of *N*-chloroacetanilide in 50 c.c. of dry benzene. Ammonia was rapidly absorbed, considerable heat was evolved, and a white solid deposited. The gas evolved was collected in a nitrometer over hydrochloric acid (1 : 1) and subsequently measured over water. In this way a quantity of nitrogen equivalent to 45·03 c.c. at N.T.P. was obtained. The equation

$$3NClPh{\cdot}CO{\cdot}CH_3 + 5NH_3 = 3NHPh{\cdot}CO{\cdot}CH_3 + 3NH_4Cl + N_2$$

requires that 1·0256 grams of acetochloroanilide should produce 45·19 c.c. of dry nitrogen at N.T.P.

α-Acetylphenylhydrazine.—This substance can be obtained in good yield by the action of sodamide on *N*-chloroacetanilide in benzene solution, provided that every precaution is taken to eliminate sodium hydroxide from the system. In the presence of sodium hydroxide, the reaction proceeds largely in the same direction as that between ammonia and *N*-chloroacetanilide, nitrogen being evolved and acetanilide regenerated.

Sodamide, prepared by the method described by Winter (*J. Amer. Chem. Soc.*, 1904, **26**, 273), was recrystallised from liquid ammonia to remove any sodium hydroxide which might be present. (Subsequently, this treatment was found to be unnecessary provided great care had been taken to exclude all sources of moisture during the preparation.) A benzene suspension of finely-divided sodamide containing 2·6 grams (1 mol.) was slowly added to a solution of 12 grams (slightly more than 1 mol.) of *N*-chloroacetanilide in dry benzene, the reaction being carried out in an atmosphere of dry hydrogen, and the temperature maintained just above the freezing point of the mixture. The flocculent mass of sodamide was rapidly replaced by more compact crystals of sodium chloride. After standing for half an hour, the reaction mixture was warmed on the water-bath for ten minutes. After the sodium chloride had been removed, the cold solution deposited a mass of brown crystals. By recrystallising these from alcohol, white needles melting at 125° were obtained. Widman (*Ber.*, 1894, **27**, 2964) gives 124—125° as the melting point of α-acetylphenylhydrazine (Found: C = 63·85; H = 6·90; N = 18·8. Calc., C = 63·97; H = 6·71; N = 18·70 per cent.).

The yield amounted to 80 per cent. calculated on the *N*-chloroacetanilide. By carrying out the reaction in liquid ammonia, using a solution of sodamide, this was increased to 85 per cent.

*α-Acetyl-*p*-tolylhydrazine* was readily obtained from *N*-chloroaceto-*p*-toluidide and sodamide in colourless plates (from benzene–light petroleum), m. p. 123° (Found: N = 16·98. Calc., N = 17·07 per cent.). The *N*-chloroaceto-*p*-toluidide was prepared according to the directions of Chattaway and Orton (T., 1900, **77**, 791) and the method of procedure was similar to that described in the case of α-acetylphenylhydrazine. About 80 per cent. of the toluidide was converted into the hydrazine. Pechmann and Runge, who prepared the same substance from phenylacetyl-*p*-tolylformazyl hydride (*Ber.*, 1894, **27**, 1698), give m. p. 122°.

α-Benzoylphenylhydrazine, prepared from sodamide and *N*-chlorobenzanilide (Chattaway and Orton, T., 1899, **75**, 1053) in the same way, crystallises from water in colourless needles melting at 70°; this is identical with the value given by Michaelis and Schmidt (*Ber.*, 1887, **20**, 43, 1713). The reaction, however, is slightly more energetic and the yield is not quite so favourable, amounting to 60 per cent.

Diacetylhydrazobenzene.—For the preparation of this substance the sodio-derivative of acetanilide was first prepared by a slight modification of the method described by Hepp (*Ber.*, 1877, **10**, 328).

4·2 Grams (1 mol.) of acetanilide were dissolved in 100 c.c. of anhydrous ether, 0·7 gram (1 atom) of sodium was added, and the mixture gently boiled until the whole of the sodium had dissolved (twelve hours). A slow stream of dry hydrogen was passed through the apparatus during this reaction. The suspension of sodioacetanilide obtained was slowly added to 5·2 grams (1 mol.) of *N*-chloroacetanilide in ether. A vigorous reaction set in and a dark red oil separated. After the ether had been removed, a current of steam was passed for a few minutes. On cooling, the residue solidified and was recrystallised from dilute alcohol, when faintly yellow, rhombic crystals were obtained melting at 105°. This is identical with the value given by Schmidt and Schultz (*Annalen*, 1881, **207**, 327) for the melting point of diacetylhydrazobenzene. The identity of the product with this substance was finally established by boiling a small quantity with concentrated hydrochloric acid for several hours, when the resulting solution yielded benzidine (m. p. 127° after recrystallisation from alcohol) on neutralisation with sodium hydroxide. The yield of diacetylhydrazobenzene amounted to 60 per cent. of the theoretical.

In concluding, I desire to express my thanks to Professor Worley for the interest which he has taken in this work.

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CLXVIII.—*Some Additive Compounds derived from Arsines.*

By GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER.

IN a previous communication (T., 1920, **117**, 1373), it was shown that tertiary arsines and halogeno-arsines combined to give additive compounds. Similarly, compounds of the type R_3As,MI_3 result when a tertiary arsine is treated with either phosphorus, arsenic, antimony, or bismuth iodide. When these additive compounds are treated with methyl iodide, their colour changes, owing to the partial formation of compounds of the type R_4AsI,MI_3. These, however, were not investigated further, since the type has already been described (Cahours and Riche, *Compt. rend.*, 1854, **39**, 541).

Arsine itself, when treated with arsenic iodide, gives no such additive compound, arsenic being the solid product obtained. Although the arsenic analogue of nitrogen iodide would therefore appear to be non-existent, an intermediate type, $AsI_3,3NH_3$, was described by Bamberger and Philipp (*Ber.*, 1881, **14**, 2644). Stibine behaves similarly to arsine (Stock and Guttmann, *Ber.*, 1904, **37**, 885).

Stannic iodide also combines with tertiary arsines, giving compounds, however, in which two molecules of the arsine are united to one of stannic iodide.

EXPERIMENTAL.

Compound $PhMe_2As,PI_3$.—When phenyldimethylarsine (1 mol.) is added to a solution of phosphorus iodide (1 mol.) in carbon disulphide, heat is evolved, and orange prisms separate. These melt at about 140°, and are very difficult to purify, owing to the ease with which the compound absorbs water (Found: I = 57·4. $C_8H_{11}I_3PAs$ requires I = 64·1 per cent.). The analysis, and the fact that the compound is formed quantitatively, are sufficient to establish the formula given, although on no occasion could an analytically pure substance be obtained.

Compound $PhMe_2As,AsI_3$.—This compound separates on mixing boiling chloroform solutions of molecular proportions of its components, and forms orange-red leaflets melting at 153° (Found: I = 59·4. $C_8H_{11}I_3As_2$ requires I = 59·7 per cent.). The compound is very sparingly soluble in the usual solvents.

Compound $PhMe_2As,SbI_3$.—Antimony iodide is dissolved in boiling benzene, and the solution treated with a molecular quantity of phenyldimethylarsine dissolved in the same solvent. Orange prisms separate, which melt at 165° and dissolve only to a slight extent in the usual solvents (Found: I = 56·2. $C_8H_{11}I_3AsSb$ requires I = 55·8 per cent.).

Compound $PhMe_2As,BiI_3$.—When an alcoholic solution containing bismuth iodide and phenyldimethylarsine in molecular proportions is boiled for a few minutes, vermilion prisms separate, melting at 198—200° (Found: Bi = 26·6. $C_8H_{11}I_3AsBi$ requires Bi = 27·0 per cent.). The compound is very sparingly soluble in the usual solvents.

Compound $2PhMe_2As,SnI_4$.—When the appropriate quantities of stannic iodide and phenyldimethylarsine are brought together in carbon disulphide solution, chocolate-coloured leaflets separate, melting at 140—145° (indef.) (Found: C = 19·6; H = 2·2; Sn = 12·0. $C_{16}H_{22}I_4As_2Sn$ requires C = 19·4; H = 2·2; Sn = 12·0 per cent.).

Phenyltrimethylarsonium Cadmi-iodide, $(PhMe_3As)_2CdI_4$.—This compound separates quantitatively as a white, crystalline precipitate (m. p. 194°) when cadmium iodide and phenyltrimethylarsonium iodide are mixed in aqueous solution (Found : I = 50·0. $C_{18}H_{28}I_4As_2Cd$ requires I = 50·1 per cent.).

Phenyldimethylethylarsonium mercuri-iodide, $PhMe_2EtAs,HgI_3$, is formed as pale yellow prisms, melting at 135°, when mercuric iodide and phenyldimethylethylarsonium iodide are brought together in aqueous acetone (Found : Hg = 25·2. $C_{10}H_{16}I_3AsHg$ requires Hg = 25·3 per cent.).

Phenyldimethylethylarsonium plumbi-iodide, $PhMe_2EtAs,PbI_3$, pale yellow prisms melting at 203°, is formed in aqueous acetone solution from lead iodide and the arsonium iodide (Found : Pb = 25·5. $C_{10}H_{16}I_3AsPb$ requires Pb = 25·9 per cent.).

The Action of Arsenic Iodide and of Iodoarsines on Tertiary Amines.

This subject has been studied with a variety of different types. Tertiary amines combine with arsenic iodide and with iodoarsines to give yellow solids, which, however, are readily hydrolysed to give the hydriodide of the base in question.

THE UNIVERSITY CHEMICAL LABORATORIES,
SYDNEY, N.S.W. [*Received, August 8th*, 1921.]

CLXIX.—*The Constitution of the Nitroprussides. Part II. The Alkylation of Nitroprussic Acid.*

By GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER.

IN a previous communication (T., 1919, **115**, 1429), it was shown that nitroprussides were derived from an acid of the molecular formula $H_2[Fe(CN)_5NO]$. The series of conductivity measurements described in the same paper has now been completed by a measurement of the conductivity of tetramethylammonium nitroprusside. Measurements of the conductivity of nitroprussic acid itself have been made, and indicate that the acid is stronger than sulphuric acid.

In addition, experiments have been carried out on the alkylation of nitroprussic acid, as a result of which diethyl nitroprusside has been isolated.

EXPERIMENTAL.

Tetramethylammonium Nitroprusside, $(Me_4N)_2[Fe(CN)_5NO]$.

This salt was prepared by treating the silver salt with the calculated quantity of tetramethylammonium iodide in aqueous solution, the filtrate from silver iodide being evaporated under diminished pressure, and the residue crystallised from alcohol. The salt forms reddish-brown leaflets, which are very soluble in water (Found: Fe = 15·3. $C_5ON_6Fe(NMe_4)_2$ requires Fe = 15·4 per cent.).

Conductivity measurements.

v.	μ.	α.
16	129·1	0·62
32	147·8	0·70
64	162·1	0·77
128	176·5	0·84
256	189·6	0·90
512	198·1	0·94
1024	205·5	0·98
∞	210	—

The comparison of these results with those previously obtained (*loc. cit.*) is of interest:

Cation.	μ_{32}.	μ_{∞}.	α_{32}.
NH_4	218·0	268·0	0·82
$MeNH_3$	185·2	240·0	0·77
Me_2NH_2	172·1	230·0	0·75
Me_3NH	154·0	212·0	0·73
Me_4N	147·8	210·0	0·70

Nitroprussic Acid, $H_2[Fe(CN)_5NO]$.

This acid was prepared by treating an aqueous solution of the barium salt with the calculated quantity of sulphuric acid, and evaporating the filtrate from barium sulphate under diminished pressure. In this way, the acid was obtained as reddish-brown leaflets, very soluble in water, giving an unstable solution (Found: Fe = 26·2. $C_5H_2ON_6Fe$ requires Fe = 25·7 per cent.).

The conductivities of various preparations were determined. The results were not entirely satisfactory, and only approximate figures could be quoted for the actual conductivity at particular dilutions. From each series of determinations, however, it was found that, in *N*/20-solution, nitroprussic acid is dissociated to the extent of about 85 per cent., and is accordingly of the same order of strength as benzenesulphonic acid.

Nitroprussic acid combines readily in aqueous solution with organic bases. Thus, the *pyridine* salt forms red needles (from alcohol) [Found: Fe = 13·0; H_2O = 12·6. $C_5ON_6Fe,(C_5H_5NH)_2,3H_2O$ requires Fe = 13·0; H_2O = 12·6 per cent.]. The *benzidine* salt is a well-defined, sparingly soluble, scarlet solid.

The Alkylation of Nitroprussic Acid.

Methyl iodide was heated in alcoholic solution, under reflux, with silver nitroprusside. A pronounced odour of isonitrile was developed, and the filtrate from silver iodide, on evaporation under diminished pressure, gave a red, hygroscopic, lachrymatory substance, which was almost certainly dimethyl nitroprusside, but it decomposed on drying, more particularly under the action of light.

A similar experiment with ethyl iodide afforded well-defined, red prisms of diethyl nitroprusside (Found: Fe = 20·0. $C_9H_{10}ON_6Fe$ requires Fe = 20·4 per cent.). The compound gives the usual reactions of a nitroprusside, and on the straightforward evidence would appear to have the formula $Et_2[Fe(CN)_5NO]$. A molecular-weight determination in water (the only cryoscopic solvent dissolving the compound) gave M = 83, 89 (two determinations) The above empirical formula requires M = 274, and it is therefore evident that diethyl nitroprusside is hydrolysed in aqueous solution to give ethyl alcohol and nitroprussic acid.

From the fact that isonitriles are invariably formed when alkyl iodides interact with complex cyanogen compounds, it seems probable that in many of these compounds, if not in all, some of the groups written as cyanogen are in reality *iso*cyanogen groups. This would afford an explanation of certain cases of isomerism, as, for example, that of the methyl ferrocyanides and cobalticyanides (Hartley, T., 1914, **105**, 521, etc.), since such isomerism may evidently be due to a difference in structure of the cyanogen radicles in the molecule, even if one adopts the simple co-ordination theory.

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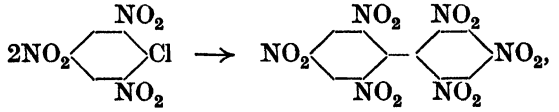
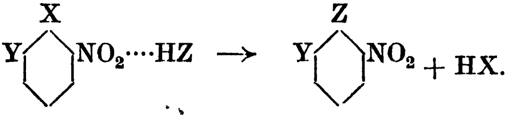
CLXX.—*The Influence of Steric Factors on Intramolecular Condensation.*

By JAMES KENNER and ERNEST WITHAM.

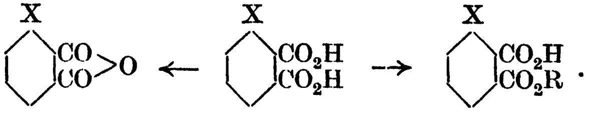
ONE of the distinguishing features of the reactions which involve the mobility of substituents in the ortho-position to a nitro-group is the comparative freedom from the steric influences usually exerted by nitro-groups. So much is this the case that the effect of introducing a second nitro- or other meta-directive group in the ortho-position is to increase, rather than to decrease, the reactivity of the mobile substituent. This is true, not merely of reactions which occur only at high temperatures, such as the formation of 2 : 4 : 6 : 2′ : 4′ : 6′-hexanitrodiphenyl from picryl chloride and copper powder (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2180),



but also of reactions which are carried out under much less drastic conditions. It has been suggested by one of us (Kenner, T., 1914, **105**, 2723) that this point is adequately explained by the view that the actual displacement of the mobile substituent is consequent on an intramolecular condensation of the preliminary compound formed through the agency of the nitro-group with the reagent employed :

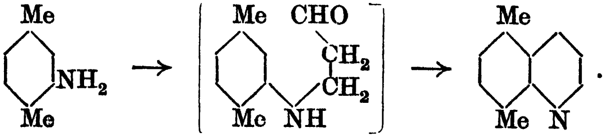


Some reactions are already on record, which suggest that steric influences do not retard intramolecular condensation to an extent comparable with their effect on intermolecular reactions. Thus, it is well known that phthalic acids of the type I form anhydrides and imides almost, if not quite, as readily as phthalic acid itself, although the ordinary processes of esterification furnish acid esters :

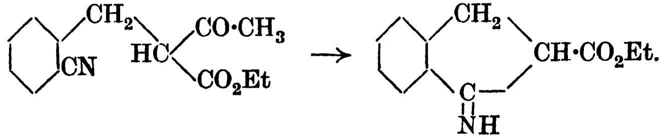


(I.)

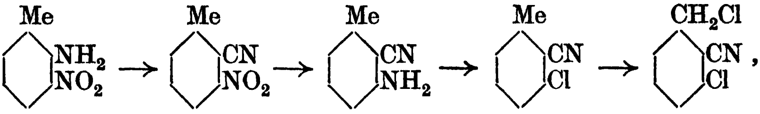
Also, there seems to be no particular difficulty in applying the Skraup reaction to *p*-xylidine (Lellmann and Alt, *Annalen*, 1887, **237**, 307) :



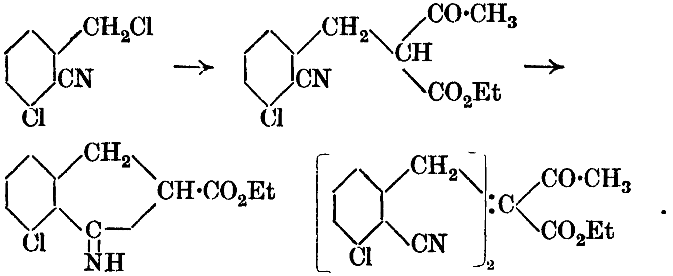
But these are isolated examples insufficient to establish the general truth of the proposition under consideration. It was therefore decided to obtain further information on this point, and as a first step in this direction to investigate a reaction in which the general conditions employed are mild. Thus the condensation of ethyl α-*o*-cyanobenzylacetoacetate to ethyl 1-iminohydrindene-2-carboxylate occurs very rapidly in alcoholic solution at 100° under the influence of a small amount of sodium ethoxide (Thorpe and Mitchell, T., 1910, **97**, 2261):



3-*Chloro-2-cyanobenzyl chloride* was therefore prepared by the series of reactions represented by the following scheme,

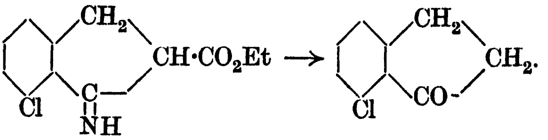


and condensed with ethyl acetoacetate under the conditions prescribed by Thorpe and Mitchell for the direct passage from *o*-cyanobenzyl chloride to the imino-compound :

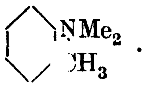


(II.)

The reaction took place readily, and after a few minutes the odour of ethyl acetate was plainly perceptible, indicating that the presence of the chlorine atom in the ortho-position to the cyanogen group had no very considerable influence on the intramolecular condensation in the second stage of the reaction. The yield of imino-compound, whilst less than that obtained by Thorpe and Mitchell in the simpler case, was satisfactory. The formation of some 20 per cent. of *ethyl* αα-bis-3-*chloro-2-cyanobenzylacetoacetate* (II) during the reaction may indicate some retarding influence of this kind, or be due to the effect of the chlorine atom in increasing the acidity of the preliminary monomolecular condensation product of the chloride with ethyl acetoacetate. The cyclic structure of *ethyl 7-chloro-1-iminohydrindene-2-carboxylate* was indicated by its conversion under the influence of dilute sulphuric acid into 7-*chloro-α-hydrindone* under the conditions employed by Thorpe and Mitchell for the preparation of the unsubstituted ketone :



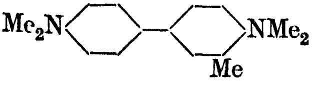
Another example is therefore supplied of the relatively slight effect of steric hindrance on intramolecular condensation. In terms of the view regarding steric hindrance originally put forward by V. Meyer, it may be said that it is inherent in the nature of such reactions, as distinguished from intermolecular condensation, that one of the ortho-substituents, instead of assisting to obstruct the mutual approach of the two condensing groups, actually tends to bring them within each other's sphere of influence. Braun (*Ber.*, 1918, **51**, 282) and Baudisch (*ibid.*, 1036; compare also Kaufmann, *ibid.*, 1907, **40**, 3999) have suggested that steric hindrance is due to a more or less complete mutual saturation by ortho-substituents of the partial valencies which effect the preliminary stages of a condensation, and represent dimethyl-*o*-toluidine by the formula (III) :

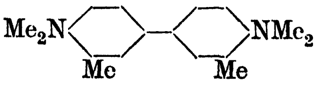


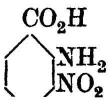
(III.)

According to this view, it would seem that intramolecular condensation should suffer some retardation from the ortho-substituent not directly concerned in the reaction, and it has been pointed out that there is some indication of this in the experiments now recorded. Further work may assist in deciding this point.

From the general evidence at present available, it may be said that cases are known to which either one or both of the theories just referred to seem to be inapplicable. The reactivity of both dimethylamino-groups in 4 : 4′-*bis*dimethylamino-3-methyldiphenyl (IV) towards cyanogen bromide and iodoacetonitrile, as contrasted with the non-reactivity of each in 4 : 4′-*bis*dimethylamino-3 : 3′-ditolyl (V) (Braun, *Ber.*, 1917, **50**, 1651) is difficult to understand from either point of view, unless perhaps with the aid of the Kaufler formula for diphenyl :

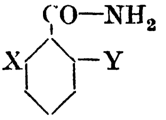




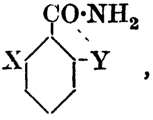


(IV.) (V.) (VI.)

The difficulty of esterifying 3-nitroanthranilic acid (VI) (James, Kenner, and Stubbings, T., 1920, **117**, 776) is at once explicable by the partial valency theory. This also satisfactorily accounts for the relatively low association of *ortho-* as compared with *meta-* and *para*-compounds, although, in the present state of our knowledge, it is equally permissible to reverse the argument, and to attribute the diminished association to steric hindrance, as indeed has already been done (Hewitt and Winmill, T., 1907, **91**, 441). On the other hand, since VII seems a more probable representation than VIII,



(VII.)

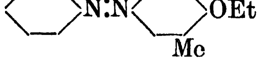


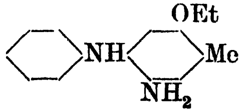
(VIII.)

it is difficult to understand how the theory of Braun and Baudisch can explain the efficacy of the Bouveault method of hydrolysing such amides by means of nitrous acid. This reaction, and the formation of esters by the action of alkyl iodides on silver salts or of methyl sulphate on sodium salts, all indicate that, in such cases, it is only the atom which is directly attached to the nucleus which suffers steric protection. The recent results of Buning (*Rec. trav. chim.*, 1921, **40**, 327) are also suggestive in this connexion, and it is possible that the esterification of sterically protected groups by the use of alcohol and excess of concentrated sulphuric acid (Wegscheider, *Ber.*, 1895, **28**, 3128; H. Meyer, *Monatsh.*, 1903, **24**, 840; 1904, **25**, 1201; Kenner and Mathews, T., 1914, **105**, 2478) is due to reactions in which the hydroxylic portion of the carboxyl group is alone concerned:

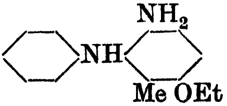
$$X{\cdot}CO_2H \longrightarrow X{\cdot}CO{\cdot}O{\cdot}SO_3H \longrightarrow X{\cdot}CO{\cdot}OR$$

Moreover, the partial valency theory does not suggest that the process of substitution is subject to steric influences, as has been at least assumed. Thus Jacobson (*Annalen*, 1895, **287**, 147) attributed to the semidine formed by the reduction of benzeneazo-*o*-cresetole the formula (X) in preference to (XI):



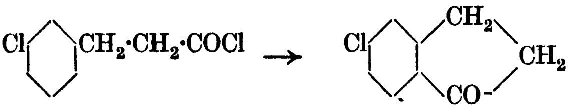


(X.)



(XI.)

and it is perhaps worth considering how far this factor is responsible for the usual predominance of para- over ortho-substitution when the two occur together. An instance of internal condensation to which this applies was observed as a supplement to the experiments above described. The application of Kipping's method for the preparation of 1-hydrindone from β-phenylpropionyl chloride (T., 1894, **65**, 480) to β-m-*chlorophenylpropionyl chloride* yielded a ketone, which was not identical with 7-chloro-1-hydrindone, and was therefore its 5-*chloro-isomeride*:



The result is, of course, not an entirely conclusive one from the point of view of steric hindrance directly, as distinguished from its possible general influence on substitution, since the chlorine atom is known to have a strongly para-directive influence in Friedel-Crafts' reactions.

Although the causes which give rise to steric hindrance are not clearly understood, and it may be necessary to seek these in some underlying feature common to the two characteristics of steric protection emphasised by the rival theories just discussed, this does not affect the fact of its constant occurrence, and the consequent necessity for allowing for its influence. In this sense, we are unable to share the regret expressed by the writer of the Annual Report on Homocyclic Compounds (1920, **17**, 72) that "it has been found necessary to have recourse to that most unsatisfactory of expedients, steric hindrance," in explaining some observations on the displacement of mobile substituents under the influence of nitro-groups. On the contrary, it is quite possible that other less important factors may also play a part. In our view, the great difficulty in elucidating the reactions of organic systems consists in properly appreciating, and in evaluating the respective importance of, all the numerous influences which operate and contribute to determine the ultimate result. Too great a concentration on what may be the conditioning factor, to the neglect of subsidiary ones, may frequently lead to conclusions quite at variance with observation. For example, consideration of the stability of cyclic structures has shown that, whilst Baeyer's original pronouncement, as generally interpreted, is broadly correct, important reservations are necessary to allow for the influence of unsaturation (Kenner and Turner, T., 1911, **99**, 2101; Kenner, T., 1913, **103**, 614) and of substitution (Kenner and Turner, *loc. cit.*; Kenner, T., 1914,

105, 2685; Beesley, Ingold, and Thorpe, T., 1915, **107**, 1080; Ingold and Thorpe, T., 1919, **115**, 320).

EXPERIMENTAL.

3-*Chloro*-2-*cyanobenzyl Chloride.*

3-Nitro-*o*-toluonitrile may be prepared in the usual manner from 3-nitro-*o*-toluidine by the Sandmeyer reaction, and isolated by steam distillation. This is a somewhat slow process, but yields a product, m. p. 115°, after crystallisation from benzene, which is purer than that obtained by the more expeditious method described by Gabriel and Thieme (*Ber.*, 1919, **52**, 1081), who give 109—110° as the melting point. Its reduction may be achieved either by means of red phosphorus and hydriodic acid (Gabriel and Thieme, *loc. cit.*), or in glacial acetic acid solution below 50° by the addition of stannous chloride in hydrochloric acid solution. It separates from benzene in long, faintly yellow prisms, m. p. 131° (Gabriel and Thieme give 127—128°).

3-*Chloro*-o-*toluonitrile*, $C_6H_3MeCl{\cdot}CN$, was prepared by the Sandmeyer reaction from 2-cyano-*m*-toluidine, a quantity of red azo-compound formed during the process of diazotisation being first removed by filtration. In spite of this, the product could not be completely freed from impurity by recrystallisation, and was therefore distilled under reduced pressure. It passed over at 143°/38 mm., and separated from light petroleum (b. p. 60—80°) in long, slender prisms, m. p. 82—83° (Found: N = 9·28. C_8H_6NCl requires N = 9·24 per cent.).

3-*Chloro*-o-*toluamide* resulted by heating a solution of the nitrile (2·3 grams) in sulphuric acid (15 c.c.) and water (5 c.c.) at 100—110° for one and a half hours, and adding the liquid to boiling water (25 c.c.). On cooling, the amide separated in scales, m. p. 167° (Found: N = 8·32. C_8H_8ONCl requires N = 8·26 per cent.).

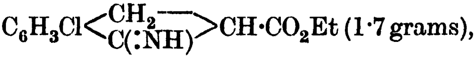
3-*Chloro*-o-*toluic acid* was obtained by careful addition of sodium nitrite in excess to a hot solution of the amide prepared in the manner just described. It crystallised from water in long, slender needles, m. p. 102° (Found: C = 56·63; H = 4·13; equivalent 170·0. $C_8H_7O_2Cl$ requires C = 56·30; H = 4·13 per cent.; equivalent 170·5).

3-*Chloro*-2-*cyanobenzyl chloride* resulted from the chlorination of 3-chloro-*o*-toluonitrile at 200° until the increase in weight was that required by theory, and was purified by repeated crystallisation from light petroleum (b. p. 60—80°). It was thus obtained in faintly yellow plates, m. p. 96°, with marked lachrymatory properties (Found: N = 7·71. $C_8H_5NCl_2$ requires N = 7·53 per cent.).

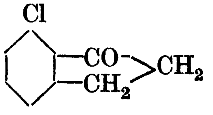
Condensation of 3-*Chloro*-2-*cyanobenzyl Chloride with Ethyl Acetoacetate.*

A solution of ethyl sodioacetoacetate, prepared by the addition of ethyl acetoacetate (3·1 grams) to a solution of sodium (0·5 gram) in alcohol (10 c.c.), was gradually added to a boiling solution of 3-chloro-2-cyanobenzyl chloride (3·95 grams) in alcohol (10 c.c.). After seven minutes the odour of ethyl acetate was easily detected, but the mixture was heated on the water-bath for a further forty-five minutes before being poured into water. The oily product did not solidify, and after being isolated by means of ether, was found to be a mixture separable into its components by treatment with cold concentrated hydrochloric acid.

The insoluble portion (1·2 grams) readily solidified, and was purified by crystallisation from dilute alcohol. In this manner, lustrous plates, m. p. 137°, were obtained, which analysis showed to be *ethyl* αα-*bis*-3-*chloro*-2-*cyanobenzylacetoacetate* (formula II) (Found: N = 6·68. $C_{22}H_{18}O_3N_2Cl_2$ requires N = 6·53 per cent.).

The hydrochloric acid solution on dilution deposited an oil which gradually solidified, the product being dried on porous earthenware. The somewhat dark *ethyl* 7-*chloro*-1-*iminohydrindene*-2-*carboxylate*,  $C_6H_3Cl{<}\substack{CH_2\text{—}\\C(:NH)}{>}CH\cdot CO_2Et$ (1·7 grams), thus obtained was crystallised from dilute alcohol, and obtained in colourless, prismatic needles, m. p. 64° (Found: N = 6·10. $C_{12}H_{12}O_2NCl$ requires N = 5·89 per cent.).

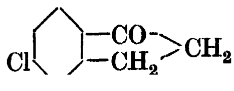
7-*Chloro*-1-*hydrindone*,



A rapid current of steam was passed through a suspension of the imino-compound just described in a large excess of 10 per cent. sulphuric acid, until the distillate was not rendered turbid by saturation with sodium chloride. The ketone was isolated in the usual manner and obtained in good yield (80 per cent. in an experiment in which it was weighed as the semicarbazone). It separates from light petroleum (b. p. 60—80°) in colourless, transparent prisms, m. p. 98° (Found: C = 64·60; H = 4·40. C_9H_7OCl requires C = 64·88; H = 4·20 per cent.).

The *semicarbazone* crystallises from alcohol in needles, m. p. 245° (decomp.) (Found: N = 18·89. $C_{10}H_{10}ON_3Cl$ requires N = 18·79 per cent.).

5-*Chloro*-1-*hydrindone*,



The authors have pleasure in acknowledging the assistance of Messrs. F. Allsop, B.Sc., T. A. Buckley, and V. A. Carpenter, B.Sc., in the earlier stages of the following preparations.

m-*Chlorobenzyl chloride* is conveniently prepared by the chlorination of *m*-chlorotoluene at its boiling point until the increase in weight amounts to about half of that required by theory. The proportion of more highly chlorinated derivatives produced is very small, and there is little difficulty in separating the desired compound as a liquid, b. p. 213—214°/740 mm. (Found : Cl in the side-chain = 22·30. $C_6H_4Cl·CH_2Cl$ requires Cl in the side-chain = 22·05 per cent.).

The condensation of *m*-chlorobenzyl chloride (49 grams) with ethyl malonate (49 grams) under the usual conditions results in the formation of *ethyl* m-*chlorobenzylmalonate*, $C_6H_4Cl·CH_2·CH(CO_2Et)_2$, (30 grams), b. p. 213—214°/40 mm. (Found : C = 59·32; H = 6·05. $C_{14}H_{16}O_4Cl$ requires C = 59·26; H = 5·64 per cent.). A large quantity of *ethyl di*-m-*chlorobenzylmalonate*, $(C_6H_4Cl·CH_2)_2C(CO_2Et)_2$, is formed at the same time, and constitutes an extremely viscous liquid, b. p. 280°/51 mm. (Found: C = 67·60; H = 5·45. $C_{21}H_{20}O_4Cl$ requires C = 67·83; H = 5·38 per cent.).

Ethyl *m*-chlorobenzylmalonate is immediately hydrolysed by alcoholic sodium hydroxide solution. m-*Chlorobenzylmalonic acid*, $C_6H_4Cl·CH_2·CH(CO_2H)_2$, crystallises from benzene in plates, m. p. 98—99° (Found : equivalent = 114·5. $C_{10}H_9O_4Cl$ requires equivalent = 114·3), and is converted at its melting point into β-m-*chlorophenylpropionic acid*, $C_6H_4Cl·CH_2·CH_2·CO_2H$, which separates from light petroleum in prismatic crystals, m. p. 73—74° (Found: equivalent = 183·9. $C_9H_9O_2Cl$ requires equivalent = 184·5). The *anilide*, $C_6H_4Cl·CH_2·CH_2·CO·NHPh$, prepared from the chloride, separates from dilute alcohol in silky needles, m. p. 86—87° (Found : N = 4·78. $C_{15}H_{14}ONCl$ requires N = 4·62 per cent.).

The conversion of β-*m*-chlorophenylpropionic acid successively into its *chloride*, b. p. 161°/39 mm., and into 5-chloro-1-hydrindone was carried out exactly as described by Kipping in the case of β-phenylpropionic acid (*loc. cit.*), very satisfactory yields being obtained at each stage.

5-*Chloro*-1-*hydrindone* crystallises from light petroleum in prisms, m. p. 96—97°, which depressed the melting point of the 7-chloro-isomeride considerably (Found: C = 64·63; H = 4·27. C_9H_7OCl requires C = 64·88; H = 4·20 per cent.).

The *semicarbazone* crystallises from alcohol in small needles, m. p. 242° (decomp.) (Found : N = 18·35. $C_{10}H_{10}ON_3Cl$ requires N = 18·79 per cent.).

The *oxime* separates from dilute alcohol in elongated plates, m. p. 148° (Found : N = 7·68. C_9H_8ONCl requires N = 7·71 per cent.).

The iso*nitroso*-derivative, prepared by treatment of the ketone in alcoholic solution with amyl nitrite and hydrochloric acid, the temperature being gradually raised to 60°, crystallises in fine needles, m. p., when rapidly heated, 232° (decomp.) (Found : N = 7·37. $C_9H_6O_2NCl$ requires N = 7·16 per cent.).

In conclusion, the authors wish to express their thanks to the British Dyestuffs Corporation for supplies of *o*-toluidine required for this investigation.

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[*Received, August 22nd*, 1921.]

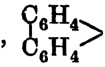
CLXXI.—9 : 10-*Dihydrophenanthrene*.

By HERBERT HENSTOCK.

IN the course of some experiments on the bromination of phenanthrene, a method was sought to absorb the hydrogen bromide formed without allowing it to escape from the reaction mixture. This object was not successfully attained, but one of the reactions seemed of interest and worthy of description on account of the formation of an almost quantitative yield of 9 : 10-dihydrophenanthrene.

A method of preparation and some of the properties of this substance have already been described by Schmidt and Mezger (*Ber.*, 1907, **40**, 4240), but their method seemed more cumbrous than the one here detailed.

The addition of the two hydrogen atoms to the phenanthrene is evidently due to the action of the hydrogen bromide, which acts in a similar manner to hydriodic acid and phosphorus.

A slight variation of the primary experiment produced a decomposition of the phenanthrene molecule with conversion into fluorenone, the glacial acetic acid used as diluent acetylating this to 9-acetoxyfluorene,  $\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!\!>\!CH\cdot O\cdot COMe$, some of the nitro- and bromo-derivatives of which have been described by Schmidt and

Bauer (*Ber.*, 1905, **38**, 3737; compare also Anschütz and Schultz, *Annalen*, 1879, **196**, 50; Meyer and Spengler, *Ber.*, 1905, **38**, 440). Schmidt and Bauer heated the nitro- and bromo-derivatives of phenanthraquinone with 10 per cent. potassium hydroxide solution, and by subsequent treatment of the products with acetic anhydride they obtained the corresponding derivatives of 9-acetoxyfluorene. The present experiment completes the reaction in one operation. The bromine used can be recovered.

EXPERIMENTAL.

A solution of 25 grams of phenanthrene (m. p. 99°) in 500 c.c. of hot glacial acetic acid containing 25 grams of fused sodium acetate was cooled to room temperature and slowly treated with a solution of 22·5 grams (1 mol.) of bromine in 150 c.c. of the same solvent with constant shaking, the mixture being cooled and kept for an hour when about one-half had been added. After standing for another hour, the whole was slowly poured, with constant stirring, into about 5 litres of water, the green, flocculent precipitate formed being filtered on the next day and dried in the air, when it weighed 50·6 grams. It contained much water, which separated after heating on a rapidly boiling water-bath for fifteen minutes; the solid portion partly crystallised on cooling, thus allowing the water to be drained off. The crude product was a light lemon-yellow, granular solid (yield 24·8 grams or 99·6 per cent.) which, after one crystallisation from suitably dilute alcohol, gave fairly pure crystals melting at 91·5° (yield 95 per cent.). Recrystallised from light petroleum, it melted at 94° and boiled at 314°. Schmidt and Mezger (*loc. cit.*) give m. p. 94–95° and b. p. 312—314° (Found: C = 73·15; H = 6·81. Calc., C = 73·33; H = 6·60 per cent.).

Examined under the microscope, the crystals were transparent, flat triangles. One or two were measured and the angles found to be each of 60°. They are therefore of the hexagonal system, being rhombohedral, hemihedral, trigonal prisms with the base {0001} strongly developed.

The substance readily sublimes to a white, crystalline solid. Its solutions exhibit a faint blue fluorescence.

The picric acid compound was obtained as yellowish-red needles melting at 138°. Schmidt and Mezger (*loc. cit.*) give 135—137° (Found: N = 10·20. Calc., N = 10·26 per cent.). It yields phenanthraquinone on oxidation with chromic acid.

Through the kind offices of Prof. H. B. Dixon the molecular weight was determined in the laboratories of the Manchester University. Using the cryoscopic method, 0·2156 in 22·507 of benzene gave Δt 0·270°, whence M = 177·4 ($C_{14}H_{12}$ requires M = 180).

It is therefore 9 : 10-dihydrophenanthrene and agrees in all its properties with the compound described by Schmidt and Mezger.

Conversion of Phenanthrene into a Fluorene Compound. 9-Acetoxyfluorene.

If in the foregoing experiment 2 mols. of bromine are used instead of 1 mol., a by-product is formed which is insoluble in light petroleum. The reaction mixture, after the addition of the bromine, was heated on the water-bath for two hours, cooled and poured into water, and the dry, crude product extracted several times with cold light petroleum, when all the dihydrophenanthrene dissolved, leaving a light green, granular solid behind (yield 4 grams). This was purified by heating on the water-bath for three hours with thrice its weight of chromic acid in glacial acetic acid, the crystals deposited on cooling being recrystallised from benzene, when the substance was obtained as thin, colourless needles melting at 272° (Found: C = 80·00; H = 5·47. Calc., C = 80·35; H = 5·35 per cent.).

The substance is oxidised neither by a chromic acid mixture, nor even on heating for six hours with sulphuric acid and potassium dichromate. It is volatile in steam, and can be sublimed without decomposition. It contains no bromine. All these properties might be expected from its constitution.

The author's thanks are due to the Research Fund Committee of the Chemical Society and also to the Government Grant Committee for grants towards the cost of the chemicals.

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CLXXII.—*The System Potassium Sulphate–Glucinum Sulphate–Water at 25°.*

By HUBERT THOMAS STANLEY BRITTON and ARTHUR JOHN ALLMAND.

THIS system has been investigated in order to ascertain the conditions necessary for the crystallisation of the double sulphate of glucinum and potassium. This salt was discovered by Awdejew in 1842 (*Pogg. Ann. Physik*, **56**, 101) in trying to isolate a salt of glucinum isomorphous with alum. He was unable to obtain any such salt from a solution containing glucinum sulphate and potassium sulphate in the ratio of three equivalents of the former to one of the latter, but was, however, successful in obtaining a double sulphate from solutions containing the constituents in molecular proportions, or in the ratio of 15 mols. of glucinum sulphate to 14 mols. of potassium sulphate. The salt crystallised out after several days. Debray (*Ann. chim. phys.*, 1855, [iii], **44**, 1), Klatzo (*J. pr. Chem.*, 1869, **106**, 227), Marignac (*Ann. chim. phys.*, 1873, [iv], **30**, 45) and Atterberg (*K. Vet.-Akad. Handl.*, 1873, **30**, (iv), 79) subsequently prepared the double sulphate and all agree to the formula assigned to it by Awdejew, namely, $K_2SO_4,GlSO_4,2H_2O$. The crystals are exceedingly small, and nobody appears to have been able to determine their form.

EXPERIMENTAL.

Preparation of Glucinum Sulphate.

Several methods were adopted for the preparation of pure glucinum sulphate from commercial glucinum nitrate.

One method used was to convert the nitrate into the oxide by strongly heating in a platinum crucible. The oxide was then dissolved by heating with moderately concentrated sulphuric acid, which slowly attacks it. Excess of sulphuric acid must be present to prevent the formation of the soluble basic sulphate. After concentration, the solution was poured into alcohol, when the alcoholic solution first became turbid and crystals of the tetrahydrate finally separated. The crystals were washed as free from sulphuric acid as possible and then recrystallised from aqueous solution.

A more convenient method was to add an excess of concentrated sulphuric acid to a concentrated solution of the nitrate. The mixture was poured into alcohol and treated as above.

The method of precipitating the hydroxide with ammonium chloride and ammonium hydroxide and dissolving the glucinum hydroxide in dilute sulphuric acid proved unsuccessful, as the precipitate retained sufficient ammonia to yield, when dissolved, a double sulphate of ammonium and glucinum. The precipitate was heated on a water-bath for several days, until it appeared perfectly dry and even then was found to contain much free ammonia, but not enough to produce the double sulphate when dissolved in sulphuric acid. The glucinum ammonium sulphate was found to be extremely deliquescent; when dried to constant weight over fused calcium chloride and analysed, it gave figures corresponding with the formula $(NH_4)_2SO_4,GlSO_4,2H_2O$ (Found: $NH_3 = 12{\cdot}44$; $SO_3 = 58{\cdot}57$; $GlO = 9{\cdot}25$. Calc., $NH_3 = 12{\cdot}46$; $SO_3 = 58{\cdot}58$; $GlO = 9{\cdot}18$ per cent.). This salt has previously been described by Atterberg (*loc. cit.*), who obtained it by concentrating over sulphuric acid a solution containing molecular proportions of the two sulphates.

The following is a typical analysis of the glucinum sulphate tetrahydrate used (Found: $GlO = 14{\cdot}10$; $SO_3 = 45{\cdot}21$. Calc., $GlO = 14{\cdot}16$; $SO_3 = 45{\cdot}17$ per cent.).

"A.R." Potassium sulphate was employed, which was found to be pure by sulphate estimations.

Methods of Analysis.

It was thought in the first instance that the amount of glucinum present in solution could most readily be found by precipitating glucinum hydroxide in the cold by ammonium chloride and ammonium hydroxide (*vide* Bleyer and Boschart, *Zeitsch. anal. Chem.*, 1912, **51**, 748). The total sulphates can be estimated as barium sulphate by the use of a solution containing much hydrochloric acid to prevent hydrolysis, and from these figures the potassium can be obtained by difference. As a check, it was proposed to evaporate known weights of solution and to ignite and weigh the residue, which would presumably consist of potassium sulphate and glucinum oxide. Glucinum sulphate can be completely converted into the oxide by strongly heating in a Bunsen flame, but the heating must be continued for three or four hours before the last traces of sulphur trioxide are driven off. This method was tried in several cases, but difficulty was experienced in getting correct results, even after heating for many hours, owing to the incomplete decomposition of the glucinum sulphate. A paper of Grahmann (*Zeitsch. anorg. Chem.*, 1913, **81**, 257), in which he works out the polytherm of the binary system potassium sulphate–glucinum sulphate, may be cited in explanation.

The precipitation of glucinum as the hydroxide has, however, the grave disadvantage that the gelatinous precipitate adsorbs much potassium sulphate, which cannot be removed by washing. It may be separated by repeated re-solution and reprecipitation, or, better, by treating the ignited precipitate with water containing enough hydrochloric acid to render the solution acid, and then precipitating any slight amount of glucinum hydroxide, which may have passed into solution in the form of potassium glucinate, with ammonium chloride and ammonium hydroxide. It has been found that the precipitate of either aluminium hydroxide or glucinum hydroxide, obtained from solutions containing either the chloride or sulphate of sodium or potassium, after ignition is always slightly alkaline to phenolphthalein. This can be accounted for by the formation of a little aluminate or glucinate. If potassium sulphate and glucinum oxide are strongly heated together, no alkalinity is produced; hence it must be inferred that the alkalinity produced when a precipitate of glucinum hydroxide containing some neutral alkali salt and some ammonium hydroxide is ignited must be due to slight interaction between the three substances.

In some cases, the amount of glucinum hydroxide is extremely small, and this makes its accurate estimation difficult. In these circumstances, it was found much more convenient to carry out the estimation of glucinum by using a modification of the titration method suggested by Bleyer and Moorman (*Zeitsch. anal. Chem.*, 1912, **51**, 360). This method was investigated as follows. Varying amounts of glucinum sulphate were dissolved in 100 c.c. of distilled water, the quantity of glucinum oxide present ranging from 0·006 gram to 0·095 gram. These solutions were titrated against 0·25*N*-sodium hydroxide until the first permanent pinkness with phenolphthalein was obtained, first at room temperature and again when boiling. The results at room temperature were low; those at 100°, for very dilute solutions (about 0·006 gram of GlO), were accurate, but gradually became low as the content of glucinum oxide increased, being as much as 4 per cent. low for a solution containing 0·09 per cent. of the oxide. The cause of these discrepancies would appear to be the carrying down of glucinum sulphate by the glucinum hydroxide. When, however, the sulphate was first converted into chloride by the addition of excess of barium chloride —say 10 c.c. of a saturated solution—accurate results by titration at 100° were obtained over the same range. When the concentration of glucinum oxide was greater than 0·1 per cent., the bulk of the precipitate of glucinum hydroxide rendered it extremely difficult to judge the end-point with accuracy. This method was also found to be satisfactory in presence of varying quantities of potassium sulphate, and was used throughout the investigation.

Equilibrium Determinations.

The procedure adopted was to make up about 100 c.c. of solution at some temperature above 25°, and to pour this into a bottle provided with a rubber stopper, through the centre of which passed the rod of a glass stirrer. The bottle was placed in a thermostat regulated at 25·0 ± 0·1°, and stirring carried on mechanically for several days until equilibrium was attained, as indicated by no further change in the composition of the solution. During this time a solid phase or phases separated out. In the case of the solution containing potassium sulphate only, the initial saturation was carried out at 80°. After the solid phase had been allowed to settle, about 20 c.c. of the liquid phase were pipetted off, weighed, and made up to 250 c.c., and portions used for analysis. The solid phase was rapidly separated by filtration on a Büchner funnel. About 5 grams were accurately weighed out, dissolved, the solution made up to 250 c.c. and analysed. Extreme care must be taken that the liquid adhering to the separated solid phase shall be typical of the liquid phase with which it was in equilibrium. This mixture is usually known as the "rest." If there is any delay in the filtration and weighing, appreciable evaporation will ensue and the "rest" will not consist of the mixture of phases which were in equilibrium. For the remainder of the system, mixtures of weighed quantities of potassium sulphate and glucinum sulphate in amounts which were thought to be slightly greater than those necessary to saturate about 100 c.c. of water at 25°, were carefully dissolved by raising the temperature by the smallest possible amount; 50° was never exceeded, as otherwise the solutions became turbid. Equilibrium was much more quickly attained when potassium sulphate crystallised out than when the double salt or glucinum sulphate crystallised out. In the case of the double salt, stirring had often to be carried on for more than a week. It is possible that the remarkable slowness with which the supersaturated solution approaches equilibrium is due to some glucinum hydroxide having been liberated. In a similar fashion, Cohen and Moesveld (*Zeitsch. phys. Chem.*, 1920, **94**, 482) found that a trace of cadmium hydroxide was sufficient to impede a saturated solution of cadmium iodide in attaining equilibrium.

The proportions of the two sulphates likely to give eutectic solutions were estimated from the results already obtained on each side of the eutectic, and by the analyses of the liquid and solid phases resulting after equilibrium had been reached, the eutectic points were determined. In the circumstances, this method was adopted in preference to the more usual procedure of making up a solution saturated with the two constituents in approximately eutectic proportions, and stirring with excess of the two solid phases which coexist in equilibrium with the mother-liquor at the invariant point. It was difficult to prepare the adequately pure double sulphate in sufficient quantity. Further, in contact with the mother-liquor, the double sulphate became pasty and formed a more or less compact mass with the other coexistent solid phase, thus making efficient stirring difficult.

The results of the analyses of the various saturated solutions and their corresponding "rests" are given in the following table.

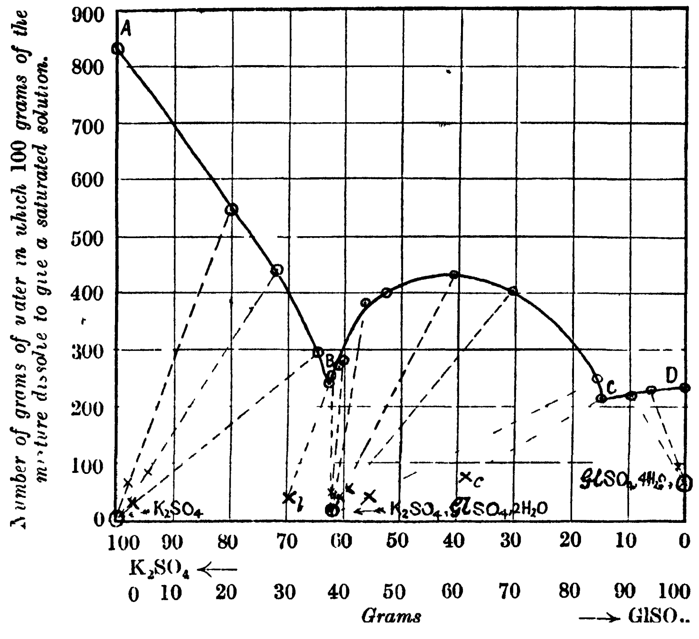
Liquid phases.			"Rests."			
Composition of 100 grams of the solute.		Grams of water in which 100 grams of the solute dissolve to form a saturated solution.	Composition of 100 grams of the anhydrous salts.		Grams of water per 100 grams of anhydrous salts.	Solid phases.
K_2SO_4.	$GlSO_4$.		K_2SO_4.	$GlSO_4$.		
100	0	830	—	—	—	K_2SO_4.
80·0	20·0	550	97·9	2·1	67	
72·0	28·0	438	94·6	5·4	84	
64·9	35·1	293	97·2	2·8	27	
62·8	37·2	241	69·7	30·3	38	K_2SO_4 and double salt.
62·3	37·7	251	62·4	37·6	17	Double salt.
61·1	38·9	264	—	—	—	
60·4	39·6	283	62·1	37·9	51	
56·7	43·3	385	61·8	38·2	42	
53·0	47·0	400	—	—	—*	
41·2	58·8	430	60·9	39·1	40	
30·8	69·2	402	59·0	41·0	57	
16·2	83·8	249	56·4	43·6	43	
15·2	84·8	218	38·3	61·7	83	$GlSO_4,4H_2O$ and double salt.
9·8	90·2	220	1·8	98·2	93	$GlSO_4,4H_2O$.
6·5	93·5	230	0	100	68·5	
0	100	234	0	100	68·5	

* In this case, the "rest" was too small to be analysed.

These results are best shown graphically, using the method of representation described by Jänecke (*Zeitsch. anorg. Chem.*, 1906, **51**, 132), the units taken being grams instead of mols. The abscissa indicates the number of grams of potassium sulphate and glucinum sulphate in 100 grams of dissolved anhydrous salts, and the ordinate shows the number of grams of water in which 100 grams of the mixture dissolve to give a saturated solution. It will be observed that the straight lines joining the points indicating the composition of the mother-liquor and the corresponding "rests" all pass through the point which indicates the composition of the solid phase with which the various liquid phases are in equilibrium.

The line *AB* represents saturated solutions which are in equilibrium with one solid phase—potassium sulphate. At *B* two solid phases—potassium sulphate and the double salt—separate out, the composition of the "rest" being shown by *b*; *B* is therefore invariant. *BC* represents saturated solutions which are in equilibrium with the double sulphate. The point *C* is invariant; the composition of its "rest," shown at *c*, indicates that the two solid phases—double sulphate and glucinum sulphate—have separated out. *CD* represents solutions which are saturated with respect to glucinum sulphate tetrahydrate.

According to this method of representation, 62·4 grams of potassium sulphate and 37·6 grams of glucinum sulphate represent molecular proportions. From the diagram it will be observed that a saturated solution of the two salts in this ratio will just be in equilibrium with the double sulphate, whereas if the amount of potassium sulphate taken happens to be slightly greater, either the two solid phases—potassium sulphate and the double salt—or potassium sulphate alone will crystallise out. Hence it becomes apparent why Awdejew found the ratio 14 mols. of potassium sulphate to 15 mols. of glucinum sulphate, that is 60·7 grams of potassium sulphate and 39·3 grams of glucinum sulphate, more satisfactory in the preparation of potassium glucinum sulphate.



Summary.

From supersaturated solutions containing potassium sulphate and glucinum sulphate, the following phases will crystallise out at 25° :

(1) K_2SO_4, if the percentage of glucinum sulphate in the solute does not exceed 37·2.

(2) $K_2SO_4,GlSO_4,2H_2O$, if the amount of glucinum sulphate in the solute lies between 37·2 and 84·8 per cent.

(3) $GlSO_4,4H_2O$, if the amount of glucinum sulphate in the solute is more than 84·8 per cent.

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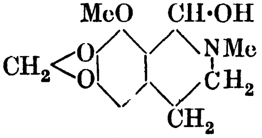
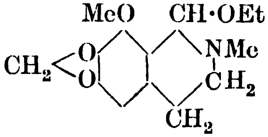
CLXXIII.—*Researches on Pseudo-bases. Part III. Dialkylaminomethyl Alkyl Ethers and Sulphides.*

By CHARLES MAXWELL MCLEOD and GERTRUDE MAUD ROBINSON.

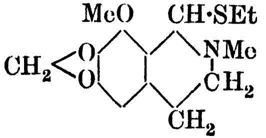
ONE of the more characteristic reactions of pseudo-basic carbinols is the formation of ethers by simple treatment with alcohols. Thus cotarnine (I) is converted into ethoxyhydrocotarnine (II) in ethyl-alcoholic solution, and when mixed with ethyl mercaptan in ethereal solution it yields ethylthiolhydrocotarnine (III) (Freund and Bamber, *Ber.*, 1902, **35**, 1752).



(I.)

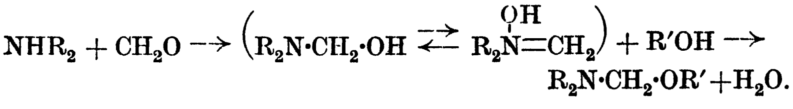


(II.)



(III.)

There are many similar instances; thus, the pseudo-basic character of berberinol is well exemplified by the formation of alkyloxydihydroberberines by treatment with alcohols (Robinson and Robinson, T., 1917, **111**, 958). It therefore seemed probable that all carbinols containing the group N·C·OH would react with alcohols with the formation of ethers, but this has apparently not yet been observed in any of the simpler conceivable cases. It is now shown that the amino-methyl alcohol derivatives which result from the action of formaldehyde on secondary bases do in fact condense with alcohols and mercaptans, yielding ethers and thio-ethers. It was found best to obtain the carbinols by the action of aqueous formaldehyde on the secondary base and then to condense with the alcohol or mercaptan in presence of an excess of potassium carbonate. The process is represented as follows :



$$NHR_2 + CH_2O \longrightarrow \left(R_2N\cdot CH_2\cdot OH \rightleftarrows R_2\overset{OH}{N}{=}CH_2\right) + R'OH \longrightarrow R_2N\cdot CH_2\cdot OR' + H_2O.$$

The yields were improved by employing only one molecular proportion of the alcohol and increased with the molecular weight of the alcohol, diethylaminomethyl *iso*amyl ether (IV) being obtained in a yield of 58 per cent. of that demanded by theory. A remarkable case is that of di(diethylaminomethyl) trimethylene ether (V), which was obtained in a yield of 92 per cent. of that demanded by theory.

$$Et_2N\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot CHMe_2$$

(IV.)

$$Et_2N\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot NEt_2.$$

(V.)

The ethers are all mobile oils which distil without decomposition and often under atmospheric pressure. They are readily soluble in the usual organic solvents, but are immiscible with water. The action of dilute hydrochloric acid causes rapid hydrolysis with formation of the original components, and the bases are also hydrolysed by water with considerably varying ease. In general, the ethers derived from alcohols of smaller molecular weight are the more readily hydrolysed, the derivatives of diethylamine are less stable than those of piperidine, and the thio-ethers are much more stable than the ethers.

At one end of the scale diethylaminoethyl ethyl ether is readily hydrolysed on shaking with cold water, and at the other diethylaminomethyl *iso*propyl sulphide is unchanged by cold water and is only slowly decomposed by hot water. The odours of all these substances are in part characteristic and in part due to the products of hydrolysis. In the case of a member of the series of intermediate stability, the first odour observed is a faint basic one; in a few seconds a powerful formaldehyde effect supervenes. It is possible that a member of this group of relatively high stability to water might have therapeutic value in view of the liberation of formaldehyde extending over a considerable period of time.

Since many of the condensation reactions of cotarnine and berberine can be made with the corresponding ethers, it was thought that some of the substances now described might be serviceable in regulated condensations designed to introduce the group $\cdot CH_2\cdot NEt_2$ in place of a hydrogen atom in suitably constituted substances. Unfortunately, the reactions do not in most cases lead to crystalline products or substances which can be distilled without decomposition, and only in two cases, condensations with acetophenone and with 2 : 4-dinitrotoluene, could evidence be obtained that the reactions of the ethers resemble those of ethoxyhydrocotarnine. Attempts were made to replace the formaldehyde in this series by benzaldehyde, but without success.

EXPERIMENTAL.

Except in those cases where a particular method of preparation is cited below, all the ethers and thio-ethers were prepared in the following manner. The secondary amine was gradually added to the aqueous solution of formaldehyde (approximately 35 per cent., termed "formalin" below) with cooling under the tap. The alcohol, glycol, or mercaptan was then introduced in one portion and the solution saturated with potassium carbonate. After shaking during an hour, the non-aqueous layer was separated and allowed to remain overnight in contact with an excess of anhydrous potassium carbonate. The product was isolated by fractionation and the ethers were in most cases so stable that this was carried out under atmospheric pressure. The equivalents of the bases were determined by decomposition with a known excess of *N*-(or *N*/10-) sulphuric acid and back-titration with *N*-(or *N*/10-)sodium hydroxide, using methyl-orange as indicator.

Diethylaminomethyl Ethyl Ether, $Et_2N\cdot CH_2\cdot OEt$.

Diethylamine (55 grams), formalin (85 grams) and ethyl alcohol (46 grams) gave 37 grams of a mobile liquid boiling at 136°/760 mm. (Found : equivalent = 130. A monoacid base, $C_7H_{17}ON$, requires equivalent = 131).

Diethylaminomethyl Propyl Ether, $Et_2N\cdot CH_2\cdot OPr$.

Diethylamine (55 grams), formalin (85 grams) and propyl alcohol (61 grams) gave 58 grams of an oil boiling at 152—155°. The pure substance boils at 152·5°/760 mm. (Found : equivalent = 144. A monoacid base, $C_8H_{19}ON$ requires equivalent = 145).

Diethylaminomethyl iso*Butyl Ether*, $Et_2N{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CHMe_2$.

Diethylamine (55 grams), formalin (85 grams), and *iso*butyl alcohol (74 grams) gave 67 grams of a base boiling at 164—167°. The main fraction was at 165°/760 mm. (Found : equivalent = 157. A monoacid base, $C_9H_{21}ON$ requires equivalent = 159).

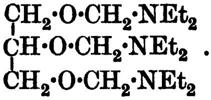
Diethylaminomethyl iso*Amyl Ether*, $Et_2N{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2$.

Diethylamine (55 grams), formalin (85 grams), and *iso*amyl alcohol (88 grams) gave 91 grams of the ether boiling at 184—188°, the correct boiling point being 186°/760 mm. (Found : $C = 69{\cdot}0$; $H = 13{\cdot}8$; equivalent = 171. A monoacid base, $C_{10}H_{23}ON$, requires $C = 69{\cdot}4$; $H = 13{\cdot}3$ per cent.; equivalent = 173).

Di(diethylaminomethyl) Trimethylene Ether, $Et_2N{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}NEt_2$.

Diethylamine (20 grams), formalin (23 grams) and trimethylene glycol (9·5 grams) gave 28·3 grams of an oil boiling at 148°/35 mm. (Found : $C = 63{\cdot}6$; $H = 12{\cdot}4$; equivalent = 123. A diacid base, $C_{13}H_{30}O_2N_2$, requires $C = 63{\cdot}4$; $H = 12{\cdot}2$ per cent.; equivalent = 123).

Tri(diethylaminomethyl) Glyceryl Ether,



$$\begin{array}{l} CH_2{\cdot}O{\cdot}CH_2{\cdot}NEt_2 \\ CH{\cdot}O{\cdot}CH_2{\cdot}NEt_2 \\ CH_2{\cdot}O{\cdot}CH_2{\cdot}NEt_2 \end{array}.$$

When the general method was applied to the case of glycerol, the only product which could be isolated was tetraethyldiaminomethane, $Et_2N{\cdot}CH_2{\cdot}NEt_2$, boiling at 168°/760 mm., and obtained in an amount almost equal to that theoretically required from the diethylamine employed. This substance remained unchanged when heated during twenty minutes at 130° with dry glycerol.* The glyceryl ether was, however, obtained under the following conditions. A mixture of glycerol (12 grams), diethylamine (22 grams), and potassium carbonate was cooled in ice-water and formalin (30 grams) gradually introduced, whilst at the same time further quantities of potassium carbonate were added when necessary so as to maintain a saturated solution. After allowing the mixture to remain overnight, the reaction was completed by heating during ten minutes on the steam-bath and the product extracted with ether after the addition of water. The ethereal solution was dried by means of potassium hydroxide and the solvent removed. The residue distilled over a wide range, but ultimately 4 grams of a basic oil boiling at 162°/33 mm. were obtained by fractionation. The substance was not soluble in water, but was readily soluble in organic solvents and on hydrolysis yielded diethylamine, formaldehyde, and glycerol (Found : equivalent = 114. A triacid base, $C_{18}H_{41}O_3N_3$ requires equivalent = 116).

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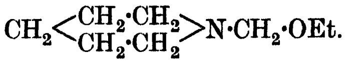
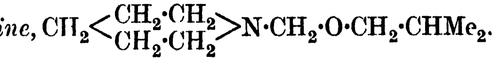
* When, however, glycerol (2 grams), tetraethyldiaminomethane (10 grams), and anhydrous sodium carbonate (3 grams) were heated together during ten minutes at 150°, 3 grams of a substance boiling at 198°/48 mm. were obtained. This was found to be also the b. p. of the glyceryl ether, and the process is therefore the better one for the preparation of the substance.



1-*Ethoxymethylpiperidine*, $CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}N\cdot CH_2\cdot OEt$.

Formalin (20 grams) was added to a mixture of piperidine (20 grams) and ethyl alcohol (45 grams) cooled by ice-water. The mixture was saturated by sodium carbonate and allowed to remain overnight, the oil being then separated, dried by sodium carbonate, and distilled, first in a vacuum and then at the atmospheric pressure; the portion boiling at 176—178°/760 mm. was collected (Found : equivalent = 141. A mono-acid base, $C_8H_{17}ON$, requires equivalent = 143).

In accordance with experience gained later, it is probable that the yield in this preparation would be improved by reducing the amount of alcohol employed to one molecular proportion.



1-iso*Butoxymethylpiperidine*, $CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}N\cdot CH_2\cdot O\cdot CH_2\cdot CHMe_2$.

Piperidine (12 grams), formalin (17 grams), and *iso*butyl alcohol (14 grams) gave 15 grams of the ether boiling at 201—203°. The boiling point of the pure substance is 203°/760 mm. (Found : equivalent = 170. A mono-acid base, $C_{10}H_{21}ON$, requires equivalent = 171).

Diethylaminomethyl Ethyl Sulphide, $Et_2N\cdot CH_2\cdot SEt$.

Diethylamine (7 grams), formalin (10·6 grams), and ethyl mercaptan (7·7 grams) gave 9·0 grams of the thio-ether boiling at 174—175°/760 mm. (Found : equivalent = 148. A mono-acid base, $C_7H_{17}NS$, requires equivalent = 147).

Diethylaminomethyl iso*Propyl Sulphide*, $Et_2N\cdot CH_2\cdot SPr$.

Diethylamine (8·5 grams), formalin (13 grams), and *iso*propyl mercaptan (11·5 grams) gave 9·0 grams of the thio-ether boiling at 186—189°, the correct boiling point being 185°/760 mm. (Found :

equivalent = 160. A mono-acid base, $C_8H_{19}NS$, requires equivalent = 161).

Condensation Reactions.

The amino-ethers described above are reactive substances which readily condense with a wide range of compounds containing an activated methyl or methylene group. In most cases, however, the products were mixtures from which individual substances could not be isolated. For example, diethylaminomethyl propyl ether reacts violently with ethyl cyanoacetate in propyl-alcoholic solution. After removal of the propyl alcohol, the chief fraction obtained on distillation boiled continuously from 140—250°/15 mm. and was obviously a complex mixture.

Definite compounds could not be isolated from the reaction products of these amino-ethers and resorcinol or 2 : 4 : 6-trinitrotoluene. It is remarkable that a boiling mixture of acetone and diethylaminomethyl *iso*butyl ether remained unchanged and no interaction occurred at the boiling point between acetone and diethylaminomethyl *iso*propyl sulphide. On the other hand, definite results were obtained with acetophenone and 2 : 4-dinitrotoluene. Acetophenone (12 grams) and diethylaminomethyl *iso*butyl ether (16 grams) in *iso*butyl alcohol (50 c.c.) were boiled during an hour under reflux. After distilling away the excess of *iso*butyl alcohol, the residue was dissolved as far as possible in 2*N*-hydrochloric acid (50 c.c.) and neutral substances removed by extraction with ether. The acid solution was separated and, after the addition of sodium hydroxide, the precipitated oily base was extracted with ether, the solution dried with potassium hydroxide, and evaporated. The residual viscid oil (8 grams) could not be induced to crystallise, but a characteristic *picrate* was prepared by adding picric acid (8 grams) dissolved in acetone (20 c.c.) to the base (6 grams) and precipitating by the addition of alcohol. The derivative crystallised from a mixture of acetone and alcohol in microscopic, triangular prisms melting at 164° with decomposition. The pure picrate was decomposed by ammonia and the base taken up in ether, but after removal of the solvent the base obtained could not be crystallised. Its *platinichloride*, prepared in the usual way, crystallised from water in pale brown, microscopic needles (Found : Pt = 24·0. $(C_{13}H_{19}ON)_2,H_2PtCl_6$ requires Pt = 23·8 per cent.).

There is thus little doubt that the product of the condensation is β-*diethylaminopropiophenone*, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2$.

A mixture of 2 : 4-dinitrotoluene (11 grams), diethylaminomethyl *iso*amyl ether (11 grams), and *iso*amyl alcohol (30 c.c.) was heated at 130° and then allowed to cool. The viscid, reddish-yellow basic product of the reaction was isolated exactly as described above for the base from acetophenone, and again could not be crystallised, but could be converted into a picrate, which not only crystallised from a mixture of alcohol and acetone in prisms melting at 164° with decomposition, but melted at the same temperature when mixed with an equal amount of the picrate from acetophenone. The two substances are, however, not identical, and differ in their crystalline habit. The picrate from dinitrotoluene crystallises in quadrilateral prisms. The substance could not be analysed owing to its highly explosive character, but the base regenerated from purified material gave a *platinichloride* crystallising from hot water in yellow needles (Found: Pt = 20·4. $(C_{12}H_{17}O_4N_3)_2,H_2PtCl_6$ requires Pt = 20·6 per cent.).

It is therefore probable that the condensation of diethylaminomethyl *iso*amyl ether and 2:4-dinitrotoluene leads to the production of 2 : 4-*dinitro*-β-*diethylaminoethylbenzene*,

$$C_6H_3(NO_2)_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2,$$

and the failure of the picrate of this substance to exhibit a lowering of melting point when mixed with the picrate of β-diethylaminopropiophenone must be attributed to the fact that these melting points are really decomposition points. The further investigation of the condensation reactions of these amino-ethers is contemplated.

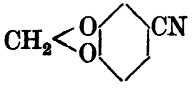
We desire to express our thanks to Professor R. Robinson, F.R.S., for suggesting this investigation and to the Food Investigation Board for grants which enabled one of us (G.M.R.) to defray a part of the cost of the materials employed.

THE UNIVERSITY OF LIVERPOOL. [*Received, August 15th,* 1921.]

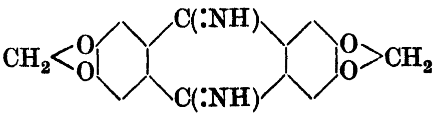
CLXXIV.—*Some Derivatives of Anthraquinonedi-imide.*

By LEON PIERRE GEORGE KEFFLER.

BROWN AND ROBINSON (T., 1917, **111**, 952) have recorded the observation that the nitrile of piperonylic acid (I) is converted in chloroform solution by chlorosulphonic acid into a polymeride which was regarded as 2 : 3 : 6 : 7-dimethylenetetraoxyanthraquinonedi-imide (II).



(I.)



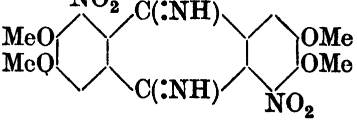
(II.)

This conclusion was based on the observed properties of the substance, the isolation of a small amount of anthracene by distillation of the product obtained by treatment with hydriodic acid with zinc dust, and on the intrinsic probability of the reaction proceeding in the direction suggested.

It appeared desirable to attempt the determination of the molecular weight of the polymeride, and all the more so in view of the fact that it is a very sparingly soluble substance which is possibly of high complexity. This was not found feasible, but the reaction occurred with equal facility when applied to veratronitrile and 3-methoxy-4-ethoxybenzonitrile, leading to analogues of the compound II, the formulæ of which are figured in the experimental portion appended. These substances were quite similar in properties to the supposed 2 : 3 : 6 : 7-dimethylenetetraoxyanthraquinonedi-imide, and were sufficiently soluble in thymol to render possible a determination of molecular weight by the cryoscopic method. The results proved conclusively that all these compounds are dimerides of the related nitriles.

These anthraquinonedi-imides are extraordinarily stable substances, and are not hydrolysed even on prolonged boiling with concentrated hydrochloric acid. They are feeble bases and are not methylated on the nitrogen by treatment with methyl sulphate in boiling nitrobenzene solution, the original substance being recovered unchanged. They are also very stable towards oxidising agents.

Dinitro-derivatives are readily obtained by treatment with cold nitric acid and dinitro-2 : 3 : 6 : 7-tetramethoxyanthraquinonedi-imide, which probably has the constitution III, has the normal molecular weight in melting thymol.



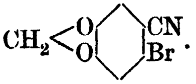
(III.)

Since it was not found possible to degrade these di-imides to simpler substances, direct proof of the orientation of the substituents could not be obtained. In almost all known cases, however, the 5-position is the reactive one in a 4-substituted catechol ether, and when this position was occupied, as, for example, in 6-bromopiperonylonitrile, the action of chlorosulphonic acid did not lead to the production of an anthraquinonedi-imide.

The fact that the anthraquinonedi-imides are quite colourless substances is in harmony with the observations of Willstätter, Mayer, and Pfannenstiehl (*Ber.*, 1904, **37**, 1494, 4605), who prepared benzoquinoneimide and benzoquinonedi-imide and found be colourless compounds.

EXPERIMENTAL.

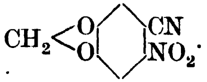
6-*Bromo*-3 : 4-*methylenedioxybenzonitrile*,



This substance has been obtained by Angeli and Rimini (*Gazzetta*, 1895, **25**, ii, 188) by an indirect method starting with safrole. It is more conveniently prepared by the dehydration of bromopiperonaldoxime. Bromopiperonal was converted into the oxime in the usual manner and this derivative crystallised from benzene. It was obtained in colourless needles, m. p. 109°, readily soluble in acetone or chloroform, but only moderately so in benzene. Bromopiperonaldoxime (50 grams) was boiled during two hours with acetic anhydride (400 grams) and the product decomposed by dilute hydrochloric acid. The nitrile crystallised from methyl alcohol in needles melting at 135° (Found : Br = 34·8. Calc., Br = 35·4 per cent.).

Angeli and Rimini (*loc. cit.*) give the melting point as 106°, and it is accordingly possible, although scarcely probable, that the substance obtained by these authors is an isomeride of that described above. The latter is readily soluble in most organic solvents and dissolves in concentrated sulphuric acid to a bright yellow solution, the colour of which is not discharged on the addition of water. Attempts to convert the substance into a dimeride were unsuccessful.

6-*Nitro*-3 : 4-*methylenedioxybenzonitrile*,



Piperonylonitrile was dissolved in ten times its weight of nitric acid (D 1·41) and allowed to remain at the temperature of the room during three hours. The solution was poured into water and the solid collected and washed with a solution of sodium carbonate. The substance is moderately readily soluble in alcohol or acetic acid and very readily so in acetone; it crystallises from alcohol in long, yellow needles melting at 144·5° (Found : N = 14·8. $C_8H_4O_4N_2$ requires N = 14·6 per cent.).

The compound dissolves in sulphuric acid to an emerald green solution which soon becomes brown, but no definite product was isolated as the result of the reaction.

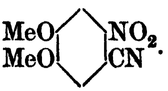
2 : 3 : 6 : 7-*Dimethylenetetraoxyanthraquinonedi-imide* (Formula II).

A series of experiments was made on the preparation of this dimeride of piperonylonitrile, but the original method of Brown and Robinson (*loc. cit.*) appears to give the best results. It was not found possible to replace the chlorosulphonic acid employed as condensing agent by concentrated sulphuric acid, oleum, dry hydrogen chloride, or such substances as phosphoryl, sulphuryl, or thionyl chloride. A yield of 30 per cent. of that theoretically possible was obtained under the following conditions. Piperonylonitrile (10 grams) was dissolved in chloroform (30 c.c.) and chlorosulphonic acid (10 c.c.) gradually added. The liquid became crimson and the temperature rose. The reaction was allowed to proceed until the mixture had cooled to the room temperature, and acetic acid (50 c.c.) and ether (100 c.c.) were then successively added. The orange solid was collected and washed with ether and then heated with a solution of sodium acetate until the colour was discharged. The precipitate was again collected, washed with water, dried, and crystallised by the addition of alcohol to its solution in nitrobenzene and then again from pyridine. The purest specimens were quite colourless needles melting at 268°. The composition was confirmed (Found : C = 65·2 ; H = 3·7 ; N = 9·6. Calc., C = 65·3 ; H = 3·4 ; N = 9·5 per cent.), but attempts to make a determination of the molecular weight were unsuccessful owing to the sparing solubility of the substance in solvents.

The Dinitro-derivative.—Dimethylenetetraoxyanthraquinonedi-imide (3 grams) was added to nitric acid (30 grams ; D 1·42) and the mixture cooled until the whole of the substance had passed into solution and its place had been taken by a new crystalline precipitate. The reaction was then completed by heating the mixture at about 50° during thirty minutes. Water was added, the solid collected, washed, dried, and crystallised from pyridine. The substance was obtained in yellow, boat-shaped, microscopic crystals which decomposed without melting above 310° (Found : C = 49·7 ; H = 2·0 ; N = 14·5. $C_{10}H_8O_8N_4$ requires C = 50·0 ; H = 2·1 ; N = 14·6 per cent.).

The substance is extremely sparingly soluble in most solvents, but it dissolves to a small extent in nitrobenzene, pyridine, or phenol. Its solution in concentrated sulphuric acid is orange.

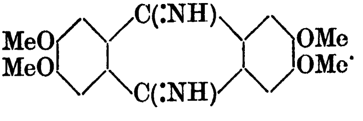
6-*Nitroveratronitrile*,



This compound was prepared by the nitration of veratronitrile (obtained in a yield of 71 per cent. by the interaction of equal weights of veratraldoxime and acetyl chloride) under the conditions described above for the production of the corresponding piperonylic derivative. The substance is readily soluble in chloroform, moderately so in alcohol or benzene, and crystallises from alcohol in yellow needles melting at 165° (Found: N = 13·6. $C_9H_8O_4N_2$ requires N = 13·5 per cent.).

The solution in sulphuric acid is green and quickly becomes brown, but the reaction appears to be complex.

2 : 3 : 6 : 7-*Tetramethoxyanthraquinonedi-imide*,



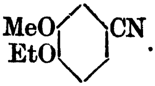
This substance was obtained by the action of chlorosulphonic acid on veratronitrile under precisely the same conditions as were employed (*vide supra*) in the preparation of the methylenedioxy-analogue, and the yield of the pure product was 26 per cent. of that theoretically possible. It crystallises well from nitrobenzene–alcohol, from xylene, and, best of all, from pyridine in slender, colourless needles melting sharply at 265°. It is extremely sparingly soluble in alcohol or ethyl acetate, moderately soluble in pyridine or nitrobenzene, and sufficiently so in melting thymol to render feasible a determination of the molecular weight by the cryoscopic method [Found: C = 66·1; H = 5·0. 0·1 (0·2) in 20·0 thymol (K = 8000) gave $\Delta t = 0{\cdot}12$ (0·25), whence M = 333 (320). $C_{18}H_{18}O_4N_2$ requires C = 66·2; H = 5·5 per cent.; M = 326].

This substance closely resembles the dimeride of piperonylonitrile and dissolves in concentrated sulphuric acid to a similar bright crimson solution, which on dilution with water becomes orange-yellow with partial precipitation of the original substance in the form of an orange salt. It dissolves in concentrated hydrochloric acid to a yellow solution, and the addition of sulphuric acid to a suspension in acetic acid also produces the orange sulphate. Such salts, which have not yet been obtained in a pure condition, are readily hydrolysed by water with production of the original weak base. All attempts to prepare the corresponding anthraquinone by hydrolysis with acids were fruitless, and the substance was recovered unchanged after boiling for some hours with concentrated hydrochloric acid. On heating with concentrated hydrochloric acid in a sealed tube at 150°, a decomposition resulted in the production of a violet-black powder of an intractable nature. Unchanged di-imide was also recovered after several hours' boiling in nitrobenzene solution with a considerable excess of methyl sulphate and anhydrous sodium carbonate. The compound was found to be quite stable towards a hot solution of potassium permanganate.

The Dinitro-derivative.—Tetramethoxyanthraquinonedi-imide (2 grams) was dissolved in nitric acid (50 grams; D 1·42). The orange solution in the course of a few minutes became cloudy, and an orange, crystalline precipitate was formed. After allowing to remain overnight, the colour of the crystals had changed to yellow, and after the addition of water the derivative was collected and crystallised from pyridine. The microscopic, spear-head-shaped, yellow crystals melted at 306° (Found: N = 13·7. 13·7. 0·1 in 20·0 thymol gave $\Delta t = 0{\cdot}095$, whence M = 421. $C_{18}H_{16}O_8N_4$ requires N = 13·5 per cent.; M = 416).

The substance is sparingly soluble in most organic solvents, and moderately soluble in hot nitrobenzene, pyridine, thymol, or phenol. It gives a reddish-brown solution in sulphuric acid. On boiling with nitric acid, the substance undergoes oxidation and further nitration, but the product was a complex mixture and could not be separated into its constituents. It was, however, proved that 4 : 5-dinitroveratrole was not among these substances, since the characteristic 2 : 3-dimethoxyphenanthraphenazine could not be obtained by reduction and subsequent condensation with phenanthraquinone. This result, taken in conjunction with the analytical data, shows that the nitro-groups are situated at positions 3 or 6 in the veratrole nuclei.

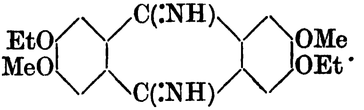
3-*Methoxy*-4-*ethoxybenzonitrile*,



Vanillonitrile was found to be readily methylated in alcoholic solution by means of methyl sulphate and potassium hydroxide, and after crystallisation from methyl alcohol the veratronitrile melted at 64° alone or mixed with a specimen obtained from veratraldoxime. The corresponding ethylation was carried out under the following conditions. Vanillonitrile (14 grams) dissolved in ethyl alcohol (100 c.c.) was converted into a sparingly soluble potassium salt by the addition of a concentrated alcoholic solution of potassium hydroxide (5 grams) and after the introduction of ethyl iodide (15·6 grams) the mixture was boiled under reflux during one and a half hours. Dilution of the cooled solution with water precipitated the product in a crystalline form, and this was collected, washed, dried, and recrystallised from alcohol, the yield amounting to 11 grams. The substance is readily soluble in most organic solvents and melts at 102° (Found: C = 68·0; H = 6·1. $C_{10}H_{11}O_2N$ requires C = 67·8; H = 6·2 per cent.).

6-*Nitro-3-methoxy-4-ethoxybenzonitrile* is readily obtained by the nitration of methoxyethoxybenzonitrile with ten times its weight of nitric acid (D 1·42). The derivative separates from the reaction mixture on standing in the cold and a further quantity is precipitated on the addition of water. The substance is sparingly soluble in the usual solvents and crystallises from pyridine in needles melting at 194°.

2 : 6-*Dimethoxy*-3 : 7-*diethoxyanthraquinonedi-imide*,



Methoxyethoxybenzonitrile (15 grams) was dissolved in chloroform (20 c.c.) and chlorosulphonic acid (20 c.c.) gradually added, the containing vessel being meanwhile surrounded by ice. After fifteen minutes, water was added and the precipitate collected, washed with boiling alcohol and crystallised from pyridine. Five grams of pure product were obtained, and this corresponds with a yield of 33·3 per cent. of that demanded by theory [Found: C = 68·2; H = 6·3. 0·1 in 20·0 thymol (K = 8000) gave Δt = 0·11, whence M = 364. $C_{20}H_{22}O_4N_2$ requires C = 67·8; H = 6·2 per cent.; M = 354].

This substance is rather more soluble than the related dimeride of veratronitrile, but is still very sparingly soluble in organic solvents of low boiling point. It crystallises from pyridine in very slender, long, colourless needles melting at 206°. Its colour reactions and other properties are almost identical with those of 2 : 3 : 6 : 7-tetramethoxyanthraquinonedi-imide. Like the latter substance, it yields a dinitro-derivative, which is very sparingly soluble and crystallises from pyridine in yellow cubes melting at 295°.

The author desires to thank Professor R. Robinson, F.R.S., for suggesting this investigation and for the interest which he has shown during its course.

THE UNIVERSITY OF LIVERPOOL. [*Received, August 20th*, 1921.]

CLXXV.—*The Determination of Surface Tension from the Rise in Capillary Tubes.*

By SAMUEL SUGDEN.

(1) *Introductory.*

THE large discrepancies between the values recorded by different observers for the surface tension of many common liquids are well known and have been the subject of much discussion. It has been shown by Richards and Coombs (*J. Amer. Chem. Soc.*, 1915, **37**, 1668) that, as far as the method of capillary rise is concerned, these discrepancies are, in many cases, due to insufficient appreciation of the approximations involved in the formula used to calculate the surface tension.

The theory of the capillary tube has been discussed by the late Lord Rayleigh (*Proc. Roy. Soc.*, 1915, [*A*], **92**, 184). For a narrow tube of radius r in which the meniscus stands at a height h above a plane surface of the liquid Rayleigh gives the equation

$$a^2 = 2\alpha^2 = r\left(h + \frac{r}{3} - 0{\cdot}1288\,\frac{r^2}{h} + 0{\cdot}1312\,\frac{r^3}{h^2}\right) \quad . \quad . \quad . \quad (1)$$

Here $$a^2 = 2\alpha^2 = \frac{2\gamma}{g(D - d)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where γ is the surface tension, g the acceleration due to gravity, D the density of the liquid, and d the density of the vapour or air and vapour if the surface tension is measured against air. This formula holds accurately as long as r/h is small compared with r, for example, for water in tubes of 1 mm. radius or less.

It was shown by Richards and Coombs that the wide tubes employed by many workers were not large enough to give a plane surface from which to measure the rise in the narrow tube and that a considerable correction for the capillary rise in the wide tube was necessary. To calculate this correction, Rayleigh (*loc. cit.*) gives the formula

$$\frac{r}{\alpha} - \log_e \frac{\alpha}{h} = 0{\cdot}8381 + 0{\cdot}2798\,\frac{\alpha}{r} + \tfrac{1}{2}\log_e \frac{r}{\alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

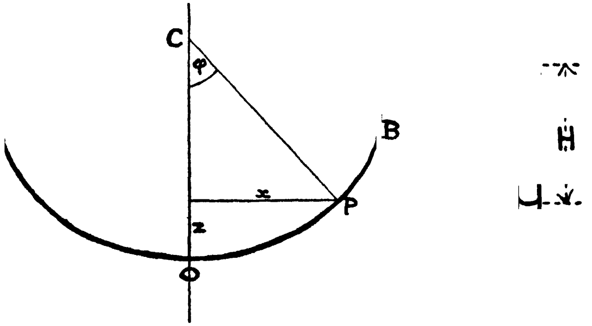
This formula may be used to calculate the capillary rise in the wider tube when r/α is greater than 6, that is, for water in tubes of 16 mm. radius or more.

The range of application of these formulæ limits the size of tube which may be used for the accurate measurement of surface tension. Richards and Carver (*J. Amer. Chem. Soc.*, 1921, **43**,

827) have used tubes of such dimensions that formulæ (1) and (3) could be employed. The use of very wide tubes, however, introduces many experimental difficulties. Large quantities of liquid are necessary, and it is not easy to measure with precision the position of the lowest point of a large meniscus which is only slightly curved.

The measurement of surface tension would be much facilitated if tubes of intermediate size could be employed and the surface tension deduced from measurements of the difference in height between two meniscuses in comparatively small tubes. Richards and Carver (*loc. cit.*) have determined experimentally the corrections for some points in this region. It is the purpose of the present paper to show that accurate values of the surface tension can be calculated from observations on any size of tube by the aid of the tables of Bashforth and Adams ("An Attempt to Test the Theory of Capillary Action," Camb. Univ. Press, 1883).

FIG. 1.



(*a*) (*b*)

(2) *The Form of the Meniscus.*

Let *AOB*, Fig. 1*a*, represent the cross section of the meniscus in a vertical cylindrical tube by a plane passing through the vertical axis of the tube *OC*. Let any point *P* on the meniscus be defined by co-ordinates *x* and *z* referred to the tangent and normal at *O* as axes. Let ϕ be the angle which the normal at *P* makes with *OC*.

The general equation to the free surface of a liquid in equilibrium under the influence of surface tension and gravity gives at *P*

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = gz(D - d) + \text{a constant} \qquad (4)$$

where R_1 and R_2 are the principal radii of curvature of the surface at P. By considering the case of $z = 0$, the constant is seen to have the value $\frac{2\gamma}{b}$, where b is the radius of curvature at O. Further, since the meniscus is a surface of revolution, one of the radii of curvature is $PC = \frac{x}{\sin\phi}$. Let ρ be the second radius of curvature; then equation 4 becomes

$$\frac{1}{\rho/b} + \frac{\sin\phi}{x/b} = 2 + \frac{g(D-d)b^2}{\gamma} \cdot z/b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This equation represents a family of curves which are determined by the value of the parameter β, where

$$\beta = \frac{g(D-d)b^2}{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

β is positive for a sessile drop, for a bubble under a plate, or for the meniscus in a vertical tube. Negative values of β correspond with the case of a pendant drop, or a pendant bubble, for example, a bubble of air escaping vertically upwards from a tube beneath the surface.

In equation 5, ρ and $\sin\phi$ may be expressed in terms of the first and second differentials of z with respect to x, but the differential equation obtained cannot be integrated. For positive values of β, Bashforth and Adams devised a special method of obtaining numerical solutions of (5) and have calculated and tabulated a large number of accurate solutions of this equation for values of β ranging from 0·1 to 100. The tables compiled by these authors are designed to facilitate the calculation of the surface tension and angle of contact from measurements of bubbles and drops. Under each value of β the values of the ratios x/b and z/b are recorded for all values of ϕ from 0° to 180° at intervals of 5°.

(3) *General Theory of the Rise of Liquids in Tubes of any Diameter.*

In Fig. 1*b* let H be the vertical distance between the lowest points of the meniscuses in two vertical tubes of radii r_1 and r_2. Let b_1 and b_2 be the radii of curvature at these points. Then from the general equation to the free surface of a liquid it follows that

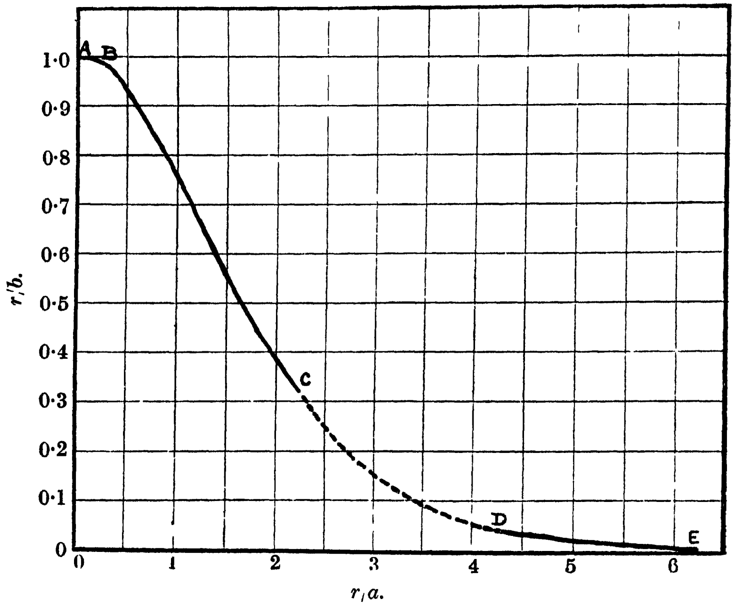
$$2\gamma\left(\frac{1}{b_1} - \frac{1}{b_2}\right) = Hg(D-d) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

To use this equation for the calculation of surface tensions, it is necessary to have some relation between the radius of the tube and the radius of curvature at the bottom of the meniscus. This relation will of necessity involve the surface tension.

The required relation for all diameters of tube is contained in Tables I and II below. These were calculated as follows.

In the first place, it was assumed that the angle of contact of the liquid with the material of the tube was zero. Richards and Carver (*loc. cit.*) have shown that this is the case for many liquids and glass. If the angle of contact is finite and is known, then the tables of Bashforth and Adams may be used as indicated below. The case of liquids with a finite angle of contact and the use of Tables I and II in connexion with Jaeger's method of measuring the surface tension will be dealt with in a further communication.

FIG. 2.



The variables chosen were r/b and r/a. If the angle of contact is zero, r/b is the x/b of Bashforth and Adams when $\phi = 90°$. (If the angle of contact is finite, then the value of x/b for the corresponding value of ϕ must be taken).

Since
$$\beta = \frac{g(D - d)b^2}{\gamma} = \frac{2b^2}{a^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$
$$\frac{r}{a} = \frac{r}{b} \cdot \sqrt{\beta/2} \, . \qquad (9)$$

hence r/a and r/b are both functions of β only and are suitable variables. As r/a increases from zero to infinity r/b decreases from unity to zero, as shown in Fig. 2.

From the tables of Bashforth and Adams, corresponding values of r/b and β were taken and r/a calculated by equation (9). Table I was constructed by careful interpolation between the numbers thus obtained. These values cover the range from $r/a = 0{\cdot}25$ to $r/a = 2{\cdot}24$. For smaller values of r/a Rayleigh's formula (1) was employed as follows.

Since Rayleigh's h is the height to which the liquid rises above a plane surface,

$$h = \frac{2\gamma}{bg(D-d)} = \frac{a^2}{b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Putting this in (1) we have

$$\frac{b}{r} = 1 + \tfrac{1}{3}\frac{r}{h} - 0{\cdot}1288\frac{r^2}{h^2} + 0{\cdot}1312\frac{r^3}{h^3} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and from (9)

$$\frac{r}{a} = \sqrt{\frac{r}{b}\cdot\frac{r}{h}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

By putting suitable values of r/h into (11) and (12) corresponding values of r/a and r/b can be calculated.

The part of the curve obtained by this method fitted smoothly on to the curve obtained from Bashforth and Adams's tables, and for a short range the two methods gave identical results. As r/a increases the last term on the right hand side of (11) increases rapidly and, as would be expected, Rayleigh's formula is no longer applicable.

Fig. 2 shows the form of curve obtained by plotting r/b against r/a. AB represents the portion calculated by Rayleigh's formula (1), BC that derived from the tables of Bashforth and Adams. DE gives the curve obtained for very wide tubes by Rayleigh's formula (3). The part of the curve represented by the broken line CD was obtained as follows. Formula (3) extrapolated to the neighbourhood of C gives values of r/b smaller than those obtained from Bashforth and Adams's tables. On the other hand a simple empirical formula

$$\frac{r}{b} = 3{\cdot}0\,\epsilon^{-r/a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

was found to agree fairly well with Rayleigh's formula from D to E, but gave rather too high values in the neighbourhood of C. Both curves were drawn on a large scale and C and D joined by a curve lying evenly between them. The values obtained in this way are recorded in Table II and are not so accurate as the values in Table I. Fortunately, accurate values are not usually needed in this region as in equation (7) the term $1/b_2$ becomes very small when r_2 is large.

The method of using the tables is best explained by means of an example. The following figures were obtained for benzene in the apparatus described in the experimental part of this paper.

$$r_1 = 0{\cdot}05495 \text{ cm.} \quad r_2 = 0{\cdot}1310 \text{ cm.}$$

At 20·0°, $H = 0{\cdot}7294$ cm.

From equation (7)

$$a^2 = \frac{H}{1/b_1 - 1/b_2}$$

As a first approximation put $b_1 = r_1$, $b_2 = r_2$.

Then $$a^2 = \frac{0{\cdot}7294}{10{\cdot}563} = 6{\cdot}905 \text{ mm.}^2$$

Using this value of a^2 to calculate r_1/a and r_2/a it is found that

$$r_1/a = 0{\cdot}2092 \text{ and } r_2/a = 0{\cdot}4987.$$

From Table I the corresponding values of r/b are

$$r_1/b = 0{\cdot}9857 \text{ and } r_2/b = 0{\cdot}9263$$

whence $$b_1 = 0{\cdot}05575 \text{ cm.}, b_2 = 0{\cdot}1415 \text{ cm.}$$

and $$a^2 = 6{\cdot}715 \text{ mm.}^2$$

Repeating the calculation with this more accurate value of a^2, it is found, as a third approximation, that

$$a^2 = 6{\cdot}701 \text{ mm.}^2$$

and further application of the method of successive approximations gives the same figure.

At 20·0°, $D = 0{\cdot}8785$ gram/cm.^{3}, $d = 0{\cdot}0014$ gram/cm.^{3}, $g = 981$ cm./sec.^{2}, whence $\gamma = 28{\cdot}83$ dynes/cm.

EXPERIMENTAL.

A simple apparatus suitable for measuring the surface tension of liquids which can only be obtained in small amounts is shown in section in Fig. 3. The essential feature is the use of two thin-walled tubes mounted close together so that both meniscuses can be seen at once in the field of view of a small reading-microscope. The eyepiece of this instrument is fitted with a travelling cross-wire moved by a micrometer screw, by means of which very accurate measurements of the distance between the two meniscuses can be made.

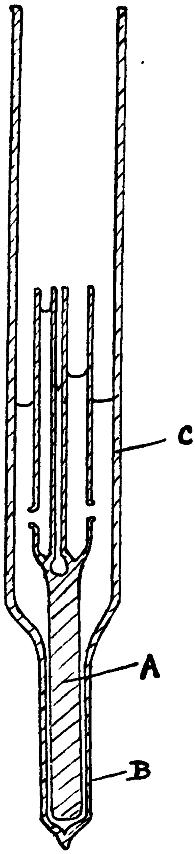
Narrow, thin-walled glass tube was found to be much more regular in bore and more nearly circular in cross section than thick-walled capillary tube, and suitable pieces were readily obtained from a stock of fine quill-tubing by submitting it to the following tests.

(*a*) The diameters at a number of different orientations at each end of a 10 cm. length of the tube were measured by means of the reading-microscope. All tubes showing a deviation from a circular cross section of more than 2 per cent. and/or a difference in diameter at the ends of more than 1 per cent. were rejected.

(*b*) Local constrictions were looked for by measuring the length of a short column of mercury in a number of positions in the tube. All the tubes which passed test (*a*) showed no appreciable variation in diameter in this test.

Two lengths of tube of suitable diameter were fused together, and a small hole was blown in the base of each. They were then cut off level about 5 cm. from the junction, and the diameter at the open end was measured accurately. The most satisfactory method of supporting this part of the apparatus in the wider tube containing the liquid is that shown in Fig. 3. The junction of the measured tubes is sealed on to a small glass rod, *A*, which slides easily into a socket, *B*, formed of narrow glass tube joined on to the lower end of the wide tube, *C*. This arrangement allows the measured tubes to be readily removed for cleaning or recalibration. The wide tube, *C*, was tested for optical irregularities by mounting a small steel ball inside it in a number of positions and measuring its vertical diameter.

FIG. 3.



Three sets of tubes were used of the following dimensions.

Apparatus 1. r_1 = 0·1343 cm. r_2 = 0·2162 cm.
„ 2. „ 0·07660 „ „ 0·1343 „
„ 3. „ 0·05495 „ „ 0·1310 „

With these instruments the surface tension of water and benzene at 20·0° was determined. These liquids were chosen so that the results could be compared directly with the figures obtained by Richards and Carver (*loc. cit.*) and Harkins and Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 499).

Tap-water and distilled water were found to give identical and consistent values, provided that the sample used was siphoned off from below the surface of the liquid which had been allowed to stand in a clean stoppered vessel for a few hours. No further purification was therefore attempted.

Benzene was freed from thiophen by standing for several days over concentrated sulphuric acid, washed with water, dried over phosphoric oxide and distilled through a long column of short lengths of glass tubing. The main fraction was submitted to several fractional crystallisations in ice, and the product dried over sodium and again distilled. The purified benzene distilled between 80·2° and 80·3°, the main fraction coming over at 80·25° (uncorr.), and had a density of 0·8785 gram/cm.^{3} at 20·0°. This figure is a little lower than that found by Perkin (T., 1896, **69**, 1191) for benzene prepared from calcium benzoate, namely, 0·8794. The difference is probably due to a trace of *cyclo*hexane which is present in coal-tar benzene and boils and freezes at almost the same temperatures as benzene. Several further crystallisations gave a small fraction of density 0·8788, showing that the impurity is only removed very slowly.

The dry benzene was found to be hygroscopic and was freshly distilled from sodium immediately before measuring the surface tension. Exposure to the air of the laboratory for a few hours invariably caused an increase of 1 to 2 per cent. in the surface tension due to the absorption of moisture, as the correct value was regained when the exposed specimen was again dried over sodium.

Before each set of measurements the apparatus was thoroughly cleaned by a hot mixture of nitric and chromic acids, washed with water, and, if necessary, dried by a current of warm, filtered air. After being rinsed with two or three lots of the liquid to be examined, the tube was filled to such a height that the meniscus in the smaller of the inner tubes rose to within a few millimetres of the open end. The apparatus was then tightly corked or sealed off and mounted approximately vertically in a thermostat at 20·0° fitted with a plate-glass window. The cross-wire of the microscope was then set vertical on a plumb-line and the apparatus adjusted until the inner tubes appeared parallel to this wire when viewed in two directions at right angles. The vertical distance between the lowest points of the two meniscuses was then measured, five settings being made, and the mean value taken.

Results.

Water was measured in instruments 1 and 2.

Apparatus.	*H.* Cm.	a^2. Sq. mm.	*D.*	*d.*	γ. Dynes per cm.
1	0·4407	14·84	0·9983	0·0012	72·59
2	0·8508	14·89	,,	,,	72·81
					Mean 72·70

Benzene was measured in instruments 2 and 3.

Apparatus.	H. Cm.	a^2. Sq. mm.	D.	d.	γ. Dynes per cm.
2	0·3924	6·708	0·8785	0·0014	28·86
3	0·7294	6·701	,,	,,	28·83
					Mean 28·85

These results are in excellent agreement with the values found by the workers previously mentioned. For water these values are 72·74 (R. and C.), 72·80 (H. and B.), and for benzene 28·88, 28·79 (R. and C.), 28·88 (H. and B.). This close agreement, however, must be regarded as fortuitous, for it is estimated that the possible errors in the measurements may amount to as much as 0·3 per cent. if they are all in the same direction.

Summary.

(1) A table of corrections has been constructed which renders possible the use of tubes of any diameter for the measurement of surface tension by the method of capillary rise.

(2) A simple form of surface tension apparatus has been devised which requires only small amounts of liquid.

(3) The surface tensions against air at 20·0° of water and benzene have been determined with the following results: Water, $\gamma = 72{\cdot}70$; benzene, $\gamma = 28{\cdot}85$ dynes per cm.

TABLE I.

Values of r/b for values of r/a from 0·00 to 2·29.

	0·00	0·01	0·02	0·03	0·04	0 05	0·06	0·07	0·08	0·09
0·00	1·0000	9999	9998	9997	9995	9992	9988	9983	9979	9974
0·10	0·9968	9960	9952	9944	9935	9925	9915	9904	9893	9881
0·20	9869	9856	9842	9827	9812	9796	9780	9763	9746	9728
0·30	9710	9691	9672	9652	9631	9610	9589	9567	9545	9522
0·40	9498	9474	9449	9424	9398	9372	9346	9320	9293	9265
0·50	9236	9208	9179	9150	9120	9090	9060	9030	8999	8968
0·60	8936	8905	8873	8840	8807	8774	8741	8708	8674	8640
0·70	8606	8571	8536	8501	8466	8430	8394	8358	8322	8286
0·80	8249	8212	8175	8138	8101	8064	8026	7988	7950	7913
0·90	7875	7837	7798	7759	7721	7683	7644	7606	7568	7529
1·00	7490	7451	7412	7373	7334	7295	7255	7216	7177	7137
1·10	7098	7059	7020	6980	6941	6901	6862	6823	6783	6744
1·20	6704	6665	6625	6586	6547	6508	6469	6431	6393	6354
1·30	6315	6276	6237	6198	6160	6122	6083	6045	6006	5968
1·40	5929	5890	5851	5812	5774	5736	5697	5659	5621	5583
1·50	5545	5508	5471	5435	5398	5362	5326	5289	5252	5216
1·60	5179	5142	5106	5070	5034	4998	4963	4927	4892	4857
1·70	4822	4787	4753	4719	4686	4652	4618	4584	4549	4514
1·80	4480	4446	4413	4380	4347	4315	4283	4250	4217	4184
1·90	4152	4120	4089	4058	4027	3996	3965	3934	3903	3873
2·00	3843	3813	3783	3753	3723	3683	3663	3633	3603	3574
2·10	3546	3517	3489	3461	3432	3403	3375	3348	3321	3294
2·20	3267	3240	3213	3186	3160	3134	3108	3082	3056	3030

TABLE II.

Values of r/b for larger values of r/a.

	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
2·0	0·384	355	327	301	276	252	229	206	185	166
3·0	149	133	119	107	097	088	081	074	067	061
4·0	056	051	047	043	039	035	031	028	025	022
5·0	020	018	017	015	014	012	010	009	008	007
6·0	006	006	005	004	004	003	003	003	002	002

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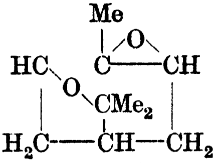
CLXXVI.—*Contributions to the Chemistry of the Terpenes. Part XX. The Action of Hypochlorous Acid on Pinene.*

By GEORGE GERALD HENDERSON and JOSEPH KENNETH MARSH.

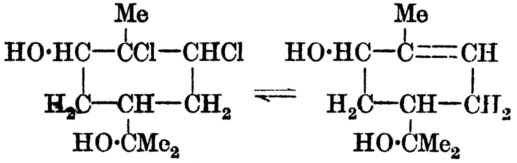
THE action of hypochlorous acid on pinene has been examined by Wagner and his collaborators (Wagner and Slawinski, *Ber.*, 1899, **32**, 2064; Wagner and Ginsberg, *Ber.*, 1896, **29**, 886; Ginsberg, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 686), but by modifying the method of carrying out the reaction we have obtained results which differ in several respects from those already published.

Wagner and Slawinski treated a cooled mixture of *l*-pinene and 10 per cent. aqueous acetic acid with a 2 per cent. aqueous solution of sodium hypochlorite in such proportions that rather more than two molecules of hypochlorous acid were present for each molecule of pinene. After completion of the reaction, the solution was separated from some undissolved oil, mixed with excess of potassium hydroxide, and, after standing for two or three days, saturated with carbon dioxide and extracted with ether. From the ethereal solution the following products were separated: a chlorohydrin, $C_{10}H_{17}O_2Cl$, m. p. 131°; traces of a different chlorohydrin; pinol oxide; sobrerythritol; nopinol glycol; and some unsaturated compounds, not further examined. Our own work has shown that these substances are not the primary products of the reaction, but are formed from these by the action of potassium hydroxide. Moreover, when Wagner and Slawinski modified their procedure by omitting the treatment of the reaction mixture with alkali hydroxide, they obtained from 300 grams of pinene about 140 grams of a viscous oil, from which they separated about 20 grams of a crystalline pinene dichlorohydrin, m. p. 136—137°; the oily residue on treatment with dilute potassium hydroxide yielded some of the chlorohydrin of m. p. 131°, and some sobrerythritol.

Treatment of pinene with successive quantities of a very dilute aqueous solution of hypochlorous acid yielded two crude products, one of which was extracted from the aqueous solution, whilst the other was insoluble in water. The soluble product proved to be a mixture of three crystalline dichlorohydrins, $C_{10}H_{18}O_2Cl_2$, which melted at 139—140°, 124—126°, and 155° respectively, together with a viscous, oily substance. The reactions of the first of these dichlorohydrins are identical with those of the compound of m. p. 136° prepared by Wagner and Slawinski, who found it to be optically active, to yield pinol oxide on treatment with aqueous potassium hydroxide, and to be converted into sobrerol when treated with zinc dust and alcohol. For these reasons, they concluded that the so-called pinene dichlorohydrin is, in fact, sobrerol dichloride or *cis*-1 : 2-dichloromenthane-6 : 8-diol,



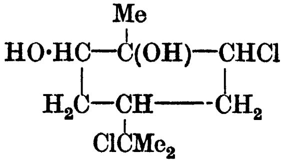
Pinol oxide.



1 : 2-Dichloromenthane-6 : 8-diol. *Sobrerol.*

We have confirmed this view of the constitution of the pinene dichlorohydrin of m. p. 139° by its direct synthesis from *i*-sobrerol by the addition of chlorine.

The second pinene dichlorohydrin, which melts at 124—126°, is optically active. Of the four possible structurally different dichlorohydrins, only two can show optical activity. One of these has been proved to be sobrerol dichloride; the other must be the compound under discussion, which therefore must be

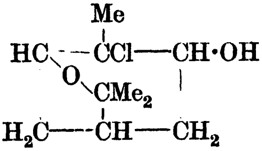


2 : 8-*Dichloromenthane*-1 : 6-*diol.*

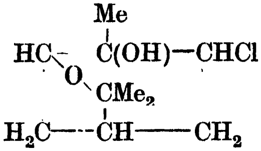
As regards the third dichlorohydrin of m. p. 155°, the quantity isolated was very small, and we have no direct evidence of its constitution. It is optically active, and may perhaps be derived from β-pinene, a little of which may possibly have been present in the specimen of pinene used.

On treatment with two molecular proportions of aqueous potassium hydroxide, the dichlorohydrin of m. p. 139° yields pinol oxide and *i*-pinol glycol 2-chlorohydrin, $C_{10}H_{17}O_2Cl$, m. p. 104—105°. The latter compound has been proved (Ginsberg and Wagner, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 675) to be the racemic form of the optically active chlorohydrin which melts at 131°. It is very stable towards aqueous potassium hydroxide in the cold, but on heating it is converted, with some resinification, into pinol oxide. On treatment with zinc dust and alcohol it yields pinol, by loss of a chlorine atom and a hydroxyl group. It cannot have the formula I

(I.)

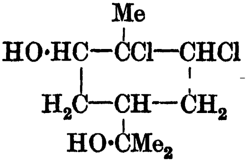


(II.)

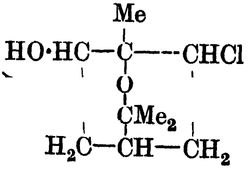


for this represents the structure of the isomeric pinol glycol 1-chlorohydrin, m. p. 52—54°, which was prepared by the action of hypochlorous acid on pinol and proved to contain a secondary alcohol group (Ginsberg, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 681). Hence it must be pinol glycol 2-chlorohydrin (II).

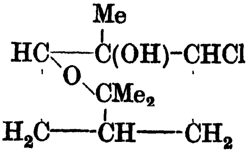
An isomeric chlorohydrin, quite different in properties from the above, is produced when the dichlorohydrin of m. p. 139° is agitated with very dilute aqueous potassium hydroxide in the proportion of 1 mol. of KOH to 1 mol. of $C_{10}H_{18}O_2Cl_2$. This substance is a crystalline solid which melts at 70—71°; the chlorine content agrees with the formula $C_{10}H_{17}O_2Cl$. Its constitution could not be directly elucidated owing to the ease with which it is transformed into the stable *i*-pinol glycol chlorohydrin of m. p. 104° by the action even of water, but in all probability it is an isomeric chlorohydrin. Indeed the conversion of pinene dichlorohydrin, m. p. 139° (III), into pinol glycol 2-chlorohydrin (V) cannot take place in a simple manner, and is more easily understood if it be assumed that the first step is the formation of this intermediate compound, for which we suggest the following formula (IV).



(III.)



(IV.)



(V.)

The fact that this intermediate compound, unlike pinol glycol 2-chlorohydrin, is capable of forming a nitrobenzoate, yields support to this view. The same formula has been suggested by Ginsberg (*loc. cit.*) for a chlorohydrin which he obtained by the action of potassium hydroxide on the syrupy product of the treatment of pinene with hypochlorous acid, but the available data are not sufficient to decide whether or not the two substances are the same.

Part of the viscous residue from which the crystalline dichlorohydrins had been separated was distilled under diminished pressure, but much decomposition took place, and no satisfactory result was obtained. Another portion, on treatment with 10 per cent. aqueous potassium hydroxide, yielded crystals of pinol glycol, m. p. 124°, which was undoubtedly formed from pinol oxide, the primary product of the action of alkali hydroxide on some dichlorohydrin still present in the residue, when the alkaline solution was acidified.

Fractional distillation under diminished pressure of the oily product which was not dissolved by water yielded some unchanged pinene and some tricyclene dichloride, $C_{10}H_{16}Cl_2$, the presence of which among the substances formed by the action of hypochlorous acid on pinene had already been observed by Ginsberg and Wagner (*loc. cit.*).

It is evident from the results quoted that the action of hypochlorous acid, even when in very dilute solution, is similar to that of many other reagents to the extent that it effects disruption of the very unstable dimethyl*cyclo*butane ring in pinene. Hence the products of the reaction are in reality derivatives of menthane and not of pinene.

EXPERIMENTAL.

Preparation of Pinene Dichlorohydrins, $C_{10}H_{18}O_2Cl_2$.

The pinene used in our experiments was prepared from American oil of turpentine by steam distillation and subsequent fractionation. It boiled at 156—157° and was slightly dextrorotatory. A dilute solution of hypochlorous acid, prepared by Taylor's method (T., 1912, **101**, 444), was shaken with a quantity of pinene in a large bottle. Absorption of the acid took place rapidly, and when complete the mixture was left until the oily layer had separated. In order to obtain good yields of the dichlorohydrins their aqueous solutions should not be kept for any long time. The aqueous layer was syphoned off and saturated with sodium chloride, with the result that part of the product separated in solid form. This was collected and the filtrate thoroughly extracted with ether. The unattacked pinene was repeatedly agitated with fresh quantities of hypochlorous acid until practically no more of the acid was taken up. As the process went on, the oily layer became by degrees denser and more viscous, developing a tendency to form emulsions, and in order to prevent this a little light petroleum was added. When the treatment with hypochlorous acid was stopped, the greater part of the original pinene had passed into solution in the water, but there remained a quantity of an oily insoluble product, which was collected and examined separately.

The mixed ethereal solutions of the soluble products were dried over anhydrous sodium sulphate, and on removal of the ether by distillation a syrupy liquid was left, from which a crystalline deposit separated on standing. The crystals were freed from the oily matter as far as possible with the aid of the filter-pump. Further deposition of crystals from the filtrate took place, and this continued for a considerable time, although separation of the crystals from the viscous oil became increasingly difficult. Finally most of the original syrupy substance was obtained in a crystalline form. The collected crops of crystals were washed with a little ether and repeatedly recrystallised from that solvent, with the result that we finally obtained a less soluble dichlorohydrin which melted at 139°, and a more soluble, of m. p. 124—126°.

Sobrerol dichloride (1 : 2-*dichloromenthane*-6 : 8-*diol*) crystallises from ether in small prisms. It melts at 139—140°, and can be distilled under diminished pressure with only slight decomposition. It is sparingly soluble in cold ether, almost insoluble in light petroleum, and very readily soluble in alcohol. In water, it dissolves rather sparingly in the cold, more easily on heating, but undergoes decomposition to some extent. It is readily attacked by cold dilute solutions of alkali hydroxides, losing a chlorine and a hydrogen atom and yielding in the first instance the chlorohydrin of m. p. 104° (Found: Cl = 29·49. $C_{10}H_{18}O_2Cl_2$ requires Cl = 29·46 per cent.).

The *nitrobenzoate*, prepared as usual in pyridine solution, is very sparingly soluble in alcohol, but is easily purified by crystallisation from a mixture of acetone and water, from which it separates as a colourless, crystalline powder which melts at 175°.

In order to confirm Wagner's view of the constitution of this dichlorohydrin, a solution of chlorine in dry chloroform was added gradually to a similar solution of sobrerol, and the solvent removed by evaporation in a vacuum desiccator. A viscous liquid remained, from which crystals separated on standing. The crystals were washed with a little ether, and after recrystallisation from that solvent were found to melt at 138°; a mixture of these with the dichlorohydrin of m. p. 139° had the same melting point.

Hence it is evident that this dichlorohydrin is really sobrerol dichloride.

The *dichlorohydrin* of m. p. 124—126°, which apparently is 2 : 8-dichloromenthane-1 : 6-diol, was separated from the isomeride just mentioned by taking advantage of its greater solubility in ether. It crystallises in colourless, silky needles, of which the solubility in water, alcohol, and light petroleum is much the same as that of sobrerol dichloride. Like the latter, it reacts readily with dilute aqueous alkali hydroxides, but it yields directly the optically active pinol glycol 2-chlorohydrin of m. p. 131°, with a trace of pinol oxide. The formation of an intermediate compound, as happens with sobrerol dichloride, was not observed under any conditions. This dichlorohydrin is lævorotatory; one specimen gave $[\alpha]_{Hg} = -28{\cdot}2°$.

A number of different fractions of crude pinene dichlorohydrin which had been prepared before the war were mixed and dissolved in hot benzene. On cooling the solution, a mass of fine, silky needles, consisting mainly of the dichlorohydrin of m. p. 124—126°, separated, together with some large, well-defined crystals. When the solution was warmed, the needles dissolved, but the bulk of the larger crystals remained behind, and was easily separated by decanting the liquid. After several recrystallisations from hot benzene, in which it is sparingly soluble, this *dichlorohydrin* was obtained in lustrous, colourless prisms melting at 155°. It is optically active, $[\alpha]_{Hg} = -59{\cdot}5°$. Like the other dichlorohydrins, it reacts with dilute aqueous alkali hydroxides, but yields a product different from either of those obtained from the former. As it appeared possible that this substance might have been formed from the dichlorohydrin of m. p. 124° by heating in benzene, this was put to the test of experiment, but even after prolonged heating the result was negative. Curiously enough, no trace of this compound could be detected in the specimens of dichlorohydrins recently prepared, although the same oil of turpentine was in each case used as the source of the pinene, and the methods of treatment were the same.

Preparation of the Chlorohydrins, $C_{10}H_{17}O_2Cl$.

12·2 Grams (1 mol.) of sobrerol dichloride were added to a 1 per cent. aqueous solution of 5·7 grams (2 mols.) of potassium hydroxide and left for four days with occasional shaking. On the third day, crystals of pinol glycol chlorohydrin separated, and on the fourth day almost all the dichlorohydrin had passed into the solution, which was now neutral. The solution was saturated with sodium chloride and extracted with ether. From the ethereal extract, 4·3 grams of a crystalline solid were obtained together with a quantity of a liquid with a strong, characteristic odour, which distilled at 78—80°/16 mm. When shaken with 2 per cent. aqueous sulphuric acid, the liquid passed into solution, and from the solution a quantity of crystals of pinol glycol, m. p. 124°, was extracted by means of ether. The liquid was thus proved to be pinol oxide. The solid product, the racemic form of pinol glycol 2-chlorohydrin, was purified by crystallisation from light petroleum, from which it separated in stout, colourless prisms, m. p. 104—105°. It is readily soluble in ether, alcohol, or acetone, from the last of which it crystallises very well, and fairly so in water, and in hot light petroleum.

When sobrerol dichloride is treated with only one proportion of potassium hydroxide, the reaction takes a different course. 16·2 Grams (1 mol.) of the dichloride, reduced to very fine powder, were added to a 0·5 per cent. aqueous solution of 3·7 grams (1 mol.) of potassium hydroxide, and the mixture was stirred continuously. In about three hours the solution had become neutral, and all but a little of the dichloride was dissolved. The solution was filtered, the filtrate saturated with sodium chloride and extracted with ether, and the ethereal extract washed with water, dried over anhydrous sodium sulphate, and distilled. There remained an oily substance which solidified after thorough drying in a vacuum desiccator, but in this case no pinol oxide was produced. The solid, which weighed 13·5 grams, was broken up, washed once or twice with a little light petroleum, and recrystallised from that solvent. When pure, this new *chlorohydrin* crystallises in radiating tufts of fine needles, which melt at 70°. It is only sparingly soluble in light petroleum, even in the heat, but dissolves very easily in other organic solvents and to some extent in water (Found: C = 58·7; H = 8·5; Cl = 17·5. $C_{10}H_{17}O_2Cl$ requires C = 58·7; H = 8·3; Cl = 17·3 per cent.).

Unlike pinol glycol chlorohydrin, this compound reacts with *p*-nitrobenzoyl chloride in pyridine solution, yielding a crystalline p-*nitrobenzoate*, which separates from alcohol in small, colourless crystals, m. p. 125°. It is very easily soluble in acetone, and sparingly soluble in alcohol.

This chlorohydrin is very easily transformed into *i*-pinol glycol chlorohydrin, m. p. 104°. The change is quickly effected if the chlorohydrin is left in contact with dilute solutions of alkali hydroxides, a little pinol oxide being also produced in this case, or if it is mixed with very dilute sulphuric acid. If an aqueous solution of the compound is left to evaporate at the ordinary temperature, crystals of *i*-pinol glycol chlorohydrin separate. It may be dissolved in glacial acetic acid without undergoing this transformation, but when an attempt was made to oxidise it with chromic anhydride in acetic acid solution, pinol glycol chlorohydrin was again produced.

The pinene dichlorohydrin of m. p. 124° was treated with one molecular proportion of potassium hydroxide in exactly the same way as sobrerol dichloride, but in no case was the chlorohydrin of m. p. 70° or any analogous intermediate compound obtained. The product consisted of the optically active pinol glycol 2-chlorohydrin, crystallising in lustrous needles of m. p. 131°, together with some of the inactive form, m. p. 104°. A trace of pinol oxide could also be detected and slight resinification occurred. This dichlorohydrin was also treated with moist silver oxide and with silver acetate in alcoholic solutions; in each case pinol oxide was produced along with a considerable amount of resinous matter. Oxidation with chromic acid mixture and with chromic anhydride in acetic acid gave no definite results, and attempts to prepare a *p*-nitrobenzoate were unsuccessful.

The Product insoluble in Water.

The oily product of the action of hypochlorous acid on pinene which remained undissolved by water was heated to remove light petroleum and then distilled at 14 mm. pressure. Fractions boiling at 80—90°, 125—130°, and 130—145° were collected. When the temperature reached 105°, decomposition began, with evolution of hydrogen chloride, and a large residue of pitchy material was left in the flask. The liquid fraction of b. p. 80—90° was redistilled under atmospheric pressure, but much decomposition ensued and no definite product, except some unchanged pinene, was isolated. The fractions of higher boiling point, principally that distilling between 125° and 130°, deposited a crystalline solid on standing, and additional quantities of this were obtained by refractionation of the liquid portions. The solid was washed with light petroleum and recrystallised. From ether, in which it is readily soluble, it separates in large, colourless plates which melt at 176°; from methyl alcohol it crystallises in leaflets, m. p. 169—172°; in cold water it is almost insoluble (Found : Cl = 34·2. $C_{10}H_{16}Cl_2$ requires Cl = 34·2 per cent.). The compound was thus identified as tricyclene dichloride, although the melting point of our specimen was higher than that (165—168°) quoted by Ginsberg and Wagner. Additional proof was provided by its conversion into camphane (Semmler, *Ber.*, 1900, **33**, 774, 3420). Tricyclene dichloride in alcoholic solution is not readily attacked by sodium, but on prolonged treatment it yielded a crystalline solid which melted at 154—155°, boiled at 160—162°, sublimed very easily in small, lustrous plates, and behaved as a saturated compound towards bromine and towards potassium permanganate; the solid, in short, was camphane.

We take this opportunity of expressing our thanks to the Department of Scientific and Industrial Research and also to the Research Fund Committee of the Carnegie Trust for grants which have defrayed the expense of this work. We wish also to acknowledge the help of Mr. J. W. Tait in some of the earlier experimental work.

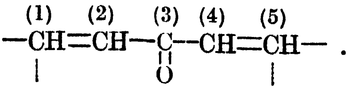
UNIVERSITY OF GLASGOW. [*Received, August 2nd*, 1921.]

CLXXVII.—*The Reactivity of Doubly-conjugated Unsaturated Ketones. Part I. 4′-Dimethylamino-2-hydroxydistyryl Ketone.*

By ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK.

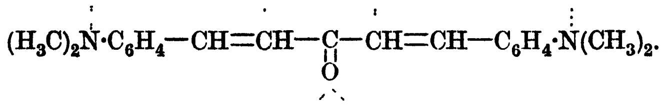
As the result of an investigation of the action of compounds possessing a reactive methylene group on ketones containing the system $\cdot C{:}C\cdot \underset{\overset{\bullet\bullet}{O}}{C}\cdot C{:}C\cdot$, such as distyryl ketone, *pp′*-tetramethyldiaminodistyryl ketone. etc., Borsche (*Annalen*, 1910, **375**, 145), basing his views on the Thiele conception of residual affinity, drew conclusions which more fully account for the varied degree of activity of these substances. Whereas distyryl ketone readily reacts with ethyl acetoacetate or acetylacetone in presence of piperidine, *pp′*-tetramethyldiaminodistyryl ketone is quite unreactive under similar conditions, whilst *p*-dimethylaminodistyryl ketone only reacts with difficulty.

According to Borsche, the reactivity of distyryl ketone is due to the large amount of free residual affinity on both the carbonyl oxygen atom and the two external carbon atoms of the conjugated system:



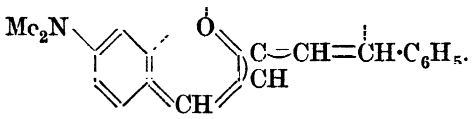
$$\underset{|}{\overset{(1)}{-CH}}=\overset{(2)}{CH}-\underset{\underset{O}{\|}}{\overset{(3)}{C}}-\overset{(4)}{CH}=\underset{|}{\overset{(5)}{CH}}-\ .$$

The inactivity of the *pp'*-tetramethyldiamino-derivative is accounted for by assuming neutralisation of the free affinities of the end carbon atoms with the unsaturated nitrogen atoms of the dimethylamino-groups.



$$(H_3C)_2\dot{N}\cdot C_6H_4-CH{=}\dot{C}H-\underset{\underset{O}{\|}}{\dot{C}}-CH{=}CH-C_6H_4\cdot\dot{N}(CH_3)_2.$$

As this, however, does not in itself explain the diminished reactivity of *p*-dimethylaminodistyryl ketone, the further assumption is made that the disturbing influence of the dimethylaminophenyl residue also affects the unsaturation of the oxygen atom in such a way that a neutralisation resulting in complex ring formation takes place :



(I.)

Although these postulates clearly demonstrate the mutual influence of groups or atoms upon each other, the explanation is not, however, complete. This may readily be demonstrated by a consideration of the above formula, where it follows that substitution in the phenyl group would not be expected to influence the activity of the molecule to any great extent, other than in the para-position, where it would tend, through neutralisation of free affinity, to cause decreased reactivity, as exhibited by *pp'*-tetramethyldiaminodistyryl ketone.

The present authors have now prepared 4'-dimethylamino-2-hydroxydistyryl ketone, and find that it actually exhibits a quite extraordinarily enhanced reactivity, being almost comparable to triphenylmethyl in the case with which it forms additive products. Before entering into a discussion of the views which we suggest in order to account for this, the preparation and properties of the substance will first be briefly discussed. By the condensation of *o*-hydroxystyryl methyl ketone with *p*-dimethylaminobenzaldehyde in alcoholic solution in presence of 10 per cent. sodium hydroxide, a deep blood-red solution is formed, which, on standing, often deposits a small quantity of an orange-red, crystalline substance melting at 194°, which is identical with *pp'*-tetramethyldiaminodistyryl ketone (Sachs and Lewin, *Ber.*, 1902, **35**, 3576).

By largely diluting the mother-liquors with water, there gradually separates out a precipitate which crystallises from alcohol in brick-red prisms melting at 143°. After removal of this substance, further dilution yields a small quantity of orange crystals, which form round the sides of the containing vessel and melt at 200°. The yield of these substances varies enormously, the reaction being extremely sensitive to very minute alterations of the conditions, such as slight variation of the room temperature or small differences of alkali concentration. In a normal reaction, the compound of m. p. 143° forms practically the total yield, but sometimes, on the other hand, none of this substance can be isolated, only a heavy tar being precipitated on dilution of the reaction mixture. In other preparations, considerable quantities of *pp'*-tetramethyldiaminodistyryl ketone resulted, even when precautions were taken to maintain the conditions as regards concentration as constant as possible. It was anticipated that the compound melting at 143° would be 4'-dimethylamino-2-hydroxydistyryl ketone, but analysis proved it to be, not the free ketone, but an additive product containing one molecule of *p*-dimethylaminobenzaldehyde. Condensation experiments were accordingly carried out, using increased quantities of *o*-hydroxystyryl methyl ketone in the hope of obtaining the free ketone, but the only effect of this was to decrease the amount of the *p*-dimethylaminobenzaldehyde additive product. Experience has shown that the highest yield of this compound is got by using 1 mol. of the ketone to 1·5 mols. of the aldehyde, when a yield equal to the weight of the *p*-dimethylaminobenzaldehyde used can be obtained.

On heating this additive compound with benzene, the brick-red crystals rapidly undergo change, without complete solution taking place, being converted into glistening, puce-coloured crystals melting at 154°. This substance is an additive product of the hydroxy-ketone with 0·5 mol. of benzene, from which it cannot be freed even on long heating at 100°. Repeated crystallisation of this benzene additive product from boiling absolute alcohol ultimately results in the replacement of the 0·5 mol. of benzene by 1 mol. of alcohol. Most other solvents appear to act similarly, an exception being ethyl acetoacetate, from which the solvent-free ketone is obtained.

The table on page 1503 gives a list of typical additive products and it will be observed that the colour of these varies from yellow to blue, green, and almost black. In certain cases, the most noticeable being in the chloroform additive product, chromotropic varieties have been isolated.

The free ketone, which is most readily obtained by heating the alcohol additive product at 100°, forms, under these conditions, a dull crimson, crystalline powder. Other coloured varieties have also been isolated by methods described in the experimental part, but the differences in colour are not especially strongly marked, and all produce a red streak. That, however, the forms are not altogether identical is shown by the fact that, whilst the brilliant scarlet variety obtained from ethyl acetoacetate readily combines in alcoholic solution with *p*-dimethylaminobenzaldehyde, the reddish-black modification obtained from ethyl acetate–heptane is unreactive. It must therefore be concluded that the free ketone can exist in different phases, and that these retain their special configuration, at least temporarily, even in solution. It consequently follows that the addenda must differ to some extent in the manner in which they are united to the ketone, and this, we consider, determines the colour of the " solvate."

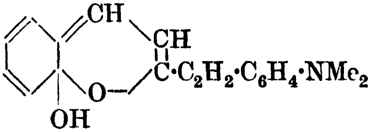
Addendum.	Composition.	Colour.
Ethyl alcohol	$C_{19}H_{19}O_2N,C_2H_6O$	purplish-black
Ethyl acetate	" $,\frac{1}{2}C_4H_8O_2$	bluish-black
Benzene	" $,C_6H_6$	almost black
	$,\frac{1}{2}C_6H_6$	puce
Chloroform	$,CHCl_3$	bright red indigo-blue
m-Dinitrobenzene	$,C_6H_4(NO_2)_2$	reddish-violet
2 : 4 : 6-Trinitrotoluene	$,2C_7H_5(NO_2)_3$	reddish-brown
p-Benzoquinone	$,C_6H_4O_2$	greenish-black
Benzene and acetic acid	$2C_{19}H\ ,O_2N,\frac{1}{2}C_6H_6,\frac{1}{2}C_2H_4O$	indigo-blue
Phenol	$C_{19}H\ ,O_2N,C_6H_5{\cdot}OH$	bluish-black
Phenanthrene	$,\frac{1}{2}C_{14}H_{10}$	emerald green
Fluorene	$,\frac{1}{2}C_{13}H_{10}$	bright green
Fluorene and methyl alcohol	$,\frac{1}{2}C_{13}H_{10},CH_3{\cdot}OH$	dark red
Carbazole	$,C_{12}H_9N$	crimson
p-Dimethylaminobenzaldehyde	" $,C_9H_{11}ON$	brick-red light yellow

pp′-*Tetramethyldiaminodistyryl Ketone.*—The presence of this substance in the condensation reaction mixture can only be accounted for by assuming a complete scission of part of the *o*-hydroxystyryl methyl ketone. In support of this, Decker and Felser (*Ber.*, 1908, **41**, 2997) have shown that both 2 : 2′-dihydroxydistyryl ketone and *o*-hydroxystyryl methyl ketone, when treated with alkali in the heat, are readily hydrolysed to salicylaldehyde and acetone. We have confirmed this, and find, further, that *o*-hydroxystyryl methyl ketone is broken up even by cold alkali of moderate concentration, the constituents then largely recombining to give 2 : 2′-dihydroxydistyryl ketone, which crystallises out in the form of its sparingly soluble sodium salt. We have further ascertained that, under similar conditions, *p*-dimethylaminostyryl methyl ketone gives the corresponding symmetrical *pp*′-tetramethyldiaminodistyryl ketone. A somewhat different type of reaction is to be recorded in the formation of *pp*′-dimethoxydistyryl ketone by the interaction of *o*-hydroxystyryl methyl ketone with anisaldehyde in the presence of alkali. Finally, a saturated alcoholic solution of the *p*-dimethylaminobenzaldehyde additive compound, when left to stand in the presence of alkali, readily yields both *pp'*-tetramethyldiaminodistyryl ketone and the substance melting at 200°. These reactions seemingly follow the ordinary laws of mass action, the tendency in all cases being towards the formation of the corresponding symmetrical and usually less soluble derivative or its salt.

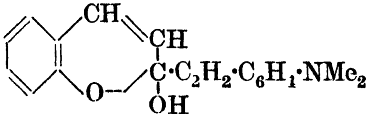
Compound Melting at 200°.—As this compound can readily be broken down by means of dilute aqueous alcohol in the heat into the hydroxy-ketone (m. p. 154°) and salicylaldehyde, experiments were accordingly undertaken to synthesise it directly from its constituents. By crystallising the free hydroxy-ketone from salicylaldehyde, deep red prisms, melting unsharply at 135°, are formed, which contain one-half molecule of salicylaldehyde. On the other hand, from an alcoholic solution of molecular proportions of the constituents, in presence of aqueous alkali, the compound melting at 200° separates out. This substance invariably contains sodium, but despite innumerable experiments having been carried out, no absolutely definite stoicheiometric relationship between the sodium and the other constituents has been established. Specimens of the product repeatedly recrystallised from absolute alcohol give analytical results which point to a compound containing one atom of sodium combined with one molecule of the hydroxy-ketone and one-half molecule of salicylaldehyde. That the production of this compound is not due to simple salt formation with the hydroxyl group of the salicylaldehyde is readily proved by the formation of completely analogous compounds from benzophenone. In absence of alkali, an additive product, melting between 137° and 143°, containing one-half molecule of benzophenone, is produced, whereas if sodium hydroxide is present a product which melts at 197° and contains approximately one atom of sodium in addition to the benzophenone is obtained. We are of the opinion that in these two compounds the sodium atom forms part of the inner complex (Formula VI), and that by its presence the salicylaldehyde or benzophenone addendum becomes more firmly attached. It is interesting to note that no sodium salt of the hydroxy-ketone itself has been isolated.

4'-Dimethylamino-2-methoxydistyryl Ketone.—In order to determine whether the outstanding properties of the hydroxy-ketone were due solely to substitution in the ortho-position or also to the specific properties of the hydroxyl group, the corresponding methyl ether was prepared. This substance, which can be obtained both in red and yellow forms melting at 95°, differs essentially in properties from the hydroxy-ketone, no longer possessing the power of forming additive products with solvents, aldehydes, *p*-benzoquinone, etc. On the other hand, it is still capable of combining with substances containing strongly negative groups, such as the polynitro-compounds.

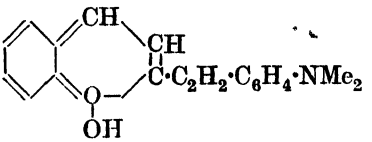
It is thus evident that the primary cause of the enhanced activity exhibited by the hydroxy-ketone is directly due to the presence of the hydroxyl group. In attempting to arrive at an explanation concerning this, the possibility of attributing different structures to the free ketone and the methyl ether was considered, for it is obviously easy to imagine a rearrangement of the ortho-substituted hydroxy-compound either into benzopyrylium bases or into an open-chain ortho-quinonoid derivative, as indicated by the following formulæ:



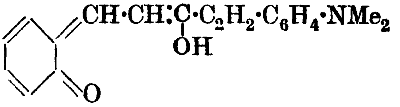
(II.)



(III.)

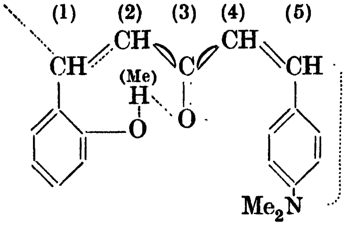


(IV.)

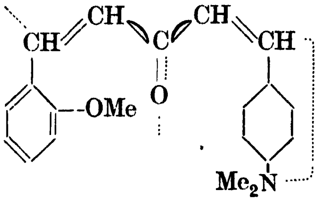


(V.)

Of these, II, III, and IV can be immediately rejected as not harmonising with the experimental results recorded in our second communication, where it is shown that the ketone forms both a hydroxylamino-derivative and a hydroxylamino-oxime (this vol., p. 1515). Similarly, V would be expected to yield only the normal oxime, but even if such a formula did actually represent the structure of the hydroxy-ketone, the difficulty would still remain, for a spectrographic examination of the two substances in alcoholic solution has shown that, in solution, at any rate, they possess identical structure, both having very similar absorption spectra with two well-defined bands at $1/\lambda = 2300$ and $3546\mu\mu$. An explanation must therefore be sought in other directions, and this we suggest may be found by taking into account, not alone the neutralisation processes advanced by Borsche (*loc. cit.*), but also the effect of such on the central carbonyl group of the crossed conjugated system. According to Pfeiffer's theory of halochromy (*Annalen*, 1910, **376**, 285; 1911, **383**, 92), the more the residual affinity of the carbonyl oxygen atom is neutralised, the more pronounced becomes the unsaturation on the carbon atom of this group. Hence, if for any reason, in *p*-dimethylaminodistyryl ketone (I), that portion of the residual affinity on the carbonyl oxygen atom not used up in the first complex ring formation were to become neutralised, more free affinity would appear on C(3). This process, we suggest, takes place in 4′-dimethylamino-2-hydroxydistyryl ketone through the formation of a second ring system involving the hydroxyl group and carbonyl oxygen atom (VI),

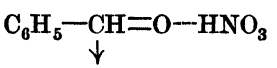


(VI.)



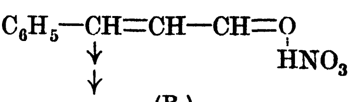
(VII.)

as a result of which the conjugated linking between C(3) and C(2) becomes intensified * at the expense of the ethenoid linking between C(2) and C(1). The final effect of this is to enhance to a very high degree the free affinity on the external atom, C(1), of the conjugated system and it is at this unsaturated centre that we consider addenda become attached in the first place. A similar conclusion has been drawn by Reddelien (*J. pr. Chem.*, 1915, [ii], **91**, 213) from his study of the additive products of nitric acid and various aldehydes and ketones. Thus, whilst benzaldehyde nitrate (A) is very unstable, the nitrate of cinnamaldehyde (B) is comparatively stable on account of the intensified partial valency.



$$C_6H_5{-}\underset{\downarrow}{CH}{=}O{-}HNO_3$$

(A.)



$$C_6H_5{-}\underset{\underset{\downarrow}{\downarrow}}{CH}{=}CH{-}CH{=}\underset{HNO_3}{\overset{}{O}}$$

(B.)

It has frequently been observed that where inner complex formation is possible the effect only becomes fully operative on the replacement of hydroxyl hydrogen by a metallic atom such as sodium. The action of alkali on 4′-dimethylamino-2-hydroxydistyryl ketone may also be interpreted as an intensification of the co-ordinated system, whereby a still higher degree of unsaturation is attained, with consequent greater stability of the partial valency additive products.

As regards the formation of a heterocyclic ring containing eight atoms, which assumption is a necessary deduction from our postulates, Werner (*Ber.*, 1908, **41**, 1062), in the development of his theory of mordant colours, suggests that the inability of phenyl *o*-hydroxystyryl ketone to form lakes with metallic bases is due to the difficulty of obtaining complex ring formation in systems in which more than six atoms are involved. It seems to us, however, that in a system where actually only five carbon atoms are involved this difficulty is more apparent than real, for it is quite conceivable that the grouping $—\mathrm{O}\overset{\mathrm{H}}{\quad}\mathrm{O}—$ approximates spatially to but one carbon atom. The ready transformation of 2 : 2′-dihydroxydistyryl ketone (VIII), on warming, into dibenzo*spiro*pyran (IX) (Decker and Felser, *loc. cit.*) would seem to support this view of close grouping.

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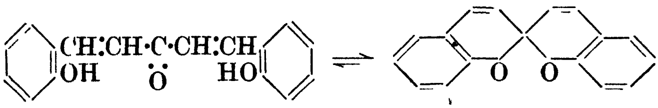
* The effect does not act between C(3) and C(4), as this whole system is in a state of equilibrium.



(VIII.) (IX.)

In the case of the methyl ether (VII) the valence distribution is substantially altered, the methoxy-group having no effect on the carbonyl oxygen atom, which consequently still retains a certain degree of free residual affinity, enabling the normal reactions of that group to become operative. In the same way, that the external carbon atom, C(1), although not possessing sufficiently enhanced free affinity to form subsidiary valence products with all addenda, is nevertheless capable of reacting in favourable circumstances, is evident from the formation of the additive compounds with dinitro- and trinitro-benzene. It is reasonable to assume that in solution 4′-dimethylamino-2-methoxydistyryl ketone is actually present as a solvate additive product.

This investigation is being extended in other directions, such as the examination both of the pyranol salts and the metallic complexes. At the same time, work is being continued with other ketones and aldehydes with the view of obtaining evidence of the effect of different substituents in the benzene nuclei.

EXPERIMENTAL.

4′-Dimethylamino-2-hydroxydistyryl Ketone + p-*Dimethylaminobenzaldehyde,*

$\mathrm{OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2,C_6H_4(NMe_2){\cdot}CHO}$.

An alcoholic solution containing 16 grams (1 mol.) of *o*-hydroxystyryl methyl ketone and 22 grams (1·5 mols.) of *p*-dimethylaminobenzaldehyde was treated with 80 c.c. of 10 per cent. sodium hydroxide (2 mols. of NaOH). The solution, which immediately acquired a blood-red colour, was kept at room temperature for two to three days and then diluted to 4000 c.c. with water. The brick-red, flocculent precipitate which gradually separated was filtered off and purified by crystallisation from absolute alcohol. The substance was obtained in thick, brick-red prisms, melting with vigorous decomposition at 143°. It is moderately soluble in methyl or ethyl alcohol or ethyl acetate, but is decomposed by benzene, chloroform, or ether. The yield obtained by the above method equals the weight of the dimethylaminobenzaldehyde taken, and is higher than that obtained when any other proportions of the constituents are used. The same product can also be obtained in shorter time, but in decreased quantity, by carrying out the reaction at 40—50°.

The Yellow Modification.—This modification can be obtained by very gradual dilution with water of an alcoholic solution of the ordinary red variety. It has also been observed in certain preparations on dilution of the original condensation mixture, but in this state it rapidly passes into the red, chromotropic form (Found: C = 75·8; H = 6·9; N = 6·3. $C_{19}H_{19}O_2N,C_9H_{11}ON$ requires C = 76·0; H = 6·8; N = 6·3 per cent.).

4′-*Dimethylamino-2-hydroxydistyryl Ketone.*

This ketone is exceedingly difficult to obtain in the free state, as it very tenaciously retains traces of solvent. It can be best prepared by heating the alcohol additive product for four hours at 100° or by triturating the benzene additive product with dry ether. Various other methods, such as recrystallisation from ethyl acetoacetate or precipitation of an ethyl acetate solution with heptane, also produce comparatively pure specimens of the hydroxy-ketone, although not entirely free from solvent. From the alcohol additive product it is obtained as a dull crimson powder melting with violent decomposition at 154°. From the benzene additive product, a light brick-red powder is formed, whereas from ethyl acetoacetate it crystallises in tiny, brilliant scarlet crystals. Black nodules giving a red streak are obtained from ethyl acetate solution by means of heptane. These different varieties show a distinct variation in activity; thus, whereas the free compound from ethyl acetoacetate readily unites in alcoholic solution with *p*-dimethylaminobenzaldehyde, the black modification, under similar conditions, does not react (Found: in product from alcohol, N = 4·79; in product from ethyl acetoacetate, N = 4·83; in product from ethyl acetate, C = 77·4; H = 6·8. $C_{19}H_{19}O_2N$ requires C = 77·8; H = 6·5; N = 4·78 per cent.).

The ketone dissolves in concentrated sulphuric acid with a deep red colour. On warming with concentrated hydrochloric acid, a red solution first forms, which rapidly changes to greenish-yellow. On gradual dilution of this solution with water, very pronounced colour phenomena are observed, the solution first becoming emerald green, then intensely violet, and finally deep indigo-blue. These colour phenomena, which are undoubtedly associated with the formation of benzopyrylium salts, are at present under investigation.

The *acetyl* derivative is readily prepared by warming the hydroxy-ketone with acetic anhydride for two hours and pouring the dark green solution into ice-water. On careful neutralisation with dilute alkali, the acetyl compound is precipitated and is finally purified by crystallisation from acetone. It forms well-defined, bright-red prisms melting at 153°, and differs essentially from the free hydroxy-ketone, no longer possessing the power of forming additive compounds with either solvents or aldehydes (Found: $N = 4{\cdot}32$. $C_{21}H_{21}O_3N$ requires $N = 4{\cdot}18$ per cent.).

o-*Methoxystyryl Methyl Ketone*, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COMe$.

This ketone was prepared with the intention of condensing it with *p*-dimethylaminobenzaldehyde to form 4′-dimethylamino-2-methoxydistyryl ketone. Harries (*Ber.*, 1891, **24**, 3180) failed to obtain this compound, but we have found that it may readily be prepared either by direct methylation of *o*-hydroxystyryl methyl ketone with methyl sulphate in aqueous alkaline solution or by condensing *o*-methoxybenzaldehyde with acetone according to Claisen's method. It forms pale yellow leaflets, m. p. 50°, b. p. 184°/10 mm. The *oxime* melts at 127° (Found: $N = 7{\cdot}35$. $C_{11}H_{13}O_4N$ requires $N = 7{\cdot}34$ per cent.).

4′-*Dimethylamino-2-methoxydistyryl Ketone*, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2$.

This compound could not be prepared either by condensation of *o*-methoxystyryl methyl ketone with *p*-dimethylaminobenzaldehyde or by direct methylation of 4′-dimethylamino-2-hydroxydistyryl ketone under ordinary conditions. It was ultimately obtained, however, in good yield by carrying out the methylation in acetone solution. 18·5 Grams of the benzene additive product, dissolved in the minimum quantity of hot acetone, were treated with 25 c.c. of 10 per cent. sodium hydroxide solution and 8·3 grams (1 mol.) of methyl sulphate added in one lot. The mixture was heated for five minutes and then diluted with water to 500 c.c., when orange nodules gradually separated. The substance crystallises from absolute alcohol in beautiful bright-red prisms melting at 95—96°. It is moderately soluble in most organic solvents and, as in the case of the acetyl derivative, it separates from these without solvent addenda. Although the ether cannot be induced to unite with either *p*-dimethylaminobenzaldehyde or salicylaldehyde, it combines readily with polynitro-hydrocarbons to yield similar additive products to those obtained from the parent substance. It dissolves in both concentrated sulphuric acid and hydrochloric acid with a red colour, which becomes green on dilution, but the intense colour changes exhibited by the parent substance do not occur.

The Yellow Modification.—On rapid recrystallisation from hot ethyl acetate, the ether is obtained in long, pale yellow needles having the same m. p. as the red form (Found : N = 4·55. $C_{20}H_{21}O_2N$ requires N = 4·56 per cent.).

Additive Products of 4′-Dimethylamino-2-hydroxydistyryl Ketone.

The general methods employed for the preparation of the additive compounds are :

(1) When the addendum is a molecule of a solvent, one of the other additive products (the benzene or chloroform compounds were generally employed) is crystallised from the required solvent, the process being repeated where necessary.

(2) Where the required addendum is a solid substance, the necessary proportions of each component are dissolved together in the minimum quantity of hot ethyl alcohol and the solution left to crystallise.

Unless otherwise stated, the melting point is the same as that of the free ketone.

Ethyl Alcohol.—$C_{19}H_{19}O_2N,C_2H_6O$ This compound crystallises as large, purplish-black aggregates of leafy prisms, with a brick-red streak (Found : N = 4·08. Calc , N = 4·13 per cent.).

Ethyl Acetate.—$C_{19}H_{19}O_2N,\frac{1}{2}C_4H_8O_2$, steely black, glistening crystalline mass (Found : N = 4·19. Calc., N = 4·17 per cent.).

Benzene.—$C_{19}H_{19}O_2N,C_6H_6$ To obtain this compound it is necessary to crystallise the hydroxy-ketone slowly from a dilute benzene solution It consists of well-formed, almost black, tapering prisms (Found : N = 3·73. Calc., N = 3·78 per cent.).

The compound $C_{19}H_{19}O_2N,\frac{1}{2}C_6H_6$, which forms a puce-coloured, crystalline powder, is obtained by boiling the *p*-dimethylaminobenzaldehyde additive compound with benzene (Found : C = 79·2 ; H = 6·8. Calc., C = 79·5 ; H = 6·6 per cent.).

Chloroform.—$C_{19}H_{19}O_2N,CHCl_3$.—*Red form* :—Bright red leaflets with a faint green lustre. This is the isomeride usually obtained from chloroform, in which, however, it is only sparingly soluble (Found: N = 3·43. Calc., N = 3·41 per cent.).

Blue form:—This modification consists of small indigo-blue crystals, and is obtained by rapidly precipitating, with vigorous scratching, a solution of the hydroxy-ketone in alcohol and chloroform, with light petroleum. It turns bright red at about 100° and reverts to the red modification without change in weight when exposed to chloroform vapour (Found: N = 3·48. Calc., N = 3·41 per cent.).

m-*Dinitrobenzene*.—$C_{19}H_{19}O_2N,C_6H_4(NO_2)_2$, reddish-violet prisms, m. p. 121—122° (Found: N = 9·10. Calc., N = 9·11 per cent.).

s-*Trinitrobenzene*.—$C_{19}H_{19}O_2N,2C_6H_3(NO_2)_3$, almost black needles giving a maroon-coloured streak. M. p. 180° (Found: N = 13·68. Calc., N = 13·64 per cent.).

2 : 4 - *Dinitrotoluene*. — $C_{19}H_{19}O_2N,C_7H_6(NO_2)_2$, reddish - violet prisms, m. p. 120—121° (Found: N = 8·5. Calc., N = 8·8 per cent.).

2 : 4 : 6-*Trinitrotoluene*.— $C_{19}H_{19}O_2N,2C_7H_5(NO_2)_3$, soft, reddish-brown aggregates, m. p. 132° (Found: N = 13·07. Calc., N = 13·1 per cent.).

p-*Benzoquinone*.—$C_{19}H_{19}O_2N,C_6H_4O_2$, small, greenish-black needles with a violet-black streak. It softens at 118° and melts completely at 144—145° (Found: C = 74·8; H = 6·1. Calc., C = 74·8; H = 5·7 per cent.).

Acetic Acid+Benzene.—$2C_{19}H_{19}O_2N,\frac{1}{2}C_6H_6,\frac{1}{2}C_2H_4O_2$. This compound is prepared by recrystallising the benzene additive product from benzene containing 20 per cent. of glacial acetic acid. The additive complex separates from the dark emerald-green solution in glistening, indigo-blue prisms (Found: C = 76·8; H = 6·8; N = 4·45. Calc., C = 76·9; H = 6·6; N = 4·3 per cent.).

Phenol.—$C_{19}H_{19}O_2N,C_6H_5{\cdot}OH$. This substance is formed by crystallising a solution of the components from a mixture of absolute alcohol and light petroleum. It forms large, well-defined, bluish-black, rhombic prisms, red in transmitted light, and gives a dull red streak. The melting point is indefinite, 120—140°, according to the rate of heating (Found: C = 77·5; H = 6·6. Calc., C = 77·6; H = 6·5 per cent.).

Phenanthrene.—$C_{19}H_{19}O_2N,\frac{1}{2}C_{14}H_{10}$, emerald green prisms with greenish-black streak. M. p. 122° (Found: C = 81·3; H = 6·4. Calc., C = 81·6; H = 6·3 per cent.).

Fluorene.—$C_{19}H_{19}O_2N,\frac{1}{2}C_{13}H_{10}$. This product is precipitated from the alcoholic solution by means of light petroleum and vigorous scratching. It forms bright green crystals with a violet-black streak. M. p. 126° (Found : C = 81·3; H = 6·5. Calc., C = 81·4; H = 6·4 per cent.).

Fluorene + Methyl Alcohol.—$C_{19}H_{19}O_2N,\frac{1}{2}C_{13}H_{10},CH_3\cdot OH$. The compound is obtained by evaporating an ethyl acetate solution of the solid components to dryness and recrystallising the residue from methyl alcohol. It forms beautiful, dark-red prisms softening at 85° and finally melting at 127° (Found : C = 77·7; H = 7·0. Calc., C = 77·9; H = 6·9 per cent.).

Carbazole.—$C_{19}H_{19}O_2N,C_{12}H_9N$, crimson crystals melting at 146° (Found : N = 6·13. Calc., N = 6·08 per cent.).

p-*Dimethylaminobenzaldehyde.*—$C_{19}H_{19}O_2N,C_9H_{11}ON$. This compound, which is readily prepared by the general method, melts at 143° and is identical in every respect with that already described.

Anisaldehyde.—$C_{19}H_{19}O_2N,\frac{1}{2}C_8H_8O_2$, dark purplish-black plates with unsharp melting point, 150—154°, and the same violent decomposition as the free ketone (Found : N = 4·1. Calc., N = 3·9 per cent.).

Salicylaldehyde.—$C_{19}H_{19}O_2N,\frac{1}{2}C_7H_6O_2$. This additive product is obtained by employing the aldehyde as solvent and allowing the solute to crystallise out. It forms small, deep-red prisms softening at 100° and melting finally at 135° (Found : C = 75·9; H = 6·5. Calc., C = 76·2; H = 6·2 per cent.).

Salicylaldehyde–Sodium Complex.—When molecular proportions of the hydroxy-ketone and salicylaldehyde are dissolved in absolute alcohol and one molecular proportion of a concentrated solution of sodium hydroxide is added, a red solid rapidly separates. By crystallisation from an alcohol–light petroleum solution, the compound is obtained as a very characteristic mass of felted, orange needles which melt at 200°. Analysis of this compound, which contains from 2- -4 per cent. of sodium, does not reveal any very exact stoicheiometric relationship between metal, ketone, and aldehyde, although the sodium content agrees comparatively well with that of a compound of the formula $C_{19}H_{18}O_2NNa,\frac{1}{2}C_7H_6O_2$. Repeated recrystallisation from the above solvent mixture brings about a gradual decrease in the sodium content, a progressive lowering of the melting point also being observed.

If absolute alcohol alone is employed as crystallising medium, well-formed, brick-red prisms which melt sharply at 196° are obtained. Further recrystallisation of these from absolute alcohol produces no depression in the melting point.

The compound is insoluble in water and is readily decomposed by boiling dilute alcohol, the free ketone being regenerated (Found : in the prismatic material, Na = 3·6; N = 3·74. $C_{19}H_{18}O_2NNa,\frac{1}{2}C_7H_6O_2$ requires Na = 3·2; N = 3·84 per cent.).

Benzophenone.—$C_{19}H_{19}O_2,\frac{1}{2}C_{13}H_{10}O$, dark red crystals with a distinct blue reflex. M. p. 137—143° (Found: C = 76·5; H = 6·8. Calc., C = 76·7; H = 6·9 per cent.).

As it was thought that possibly the sodium of the salicylaldehyde additive product had replaced the hydrogen of the phenolic hydroxyl group of the aldehyde, similar experiments were carried out with benzophenone in place of salicylaldehyde. After the addition of the alkali, the mixture rapidly solidified to a crimson mass of felted needles, which were first recrystallised from absolute alcohol and then from a mixture of alcohol and light petroleum. The product forms soft masses of felted orange needles, very similar in appearance to the salicylaldehyde–sodium additive product. It melts at 197°, which is almost the same temperature as the m. p. of the salicylaldehyde product. Results of analysis indicate that the sodium content approximates to one atom, calculated for $C_{19}H_{18}O_2NNa,C_{13}H_{10}O$ (Found: Na = 4·9; N = 3·39. Calc., Na = 5·7; N = 3·36 per cent.). Owing to the great difficulty of purification, it seems almost impossible to get concordant results with different specimens, as the sodium content can vary within wide limits, and this noticeably influences the character of the product. It would seem to be definitely established, however, that we are dealing here with a novel type of compound, which we hope to investigate in detail, and also the effect of other metals.

Curiously enough, no additive products could be obtained with naphthalene, anthracene, or *s*-trinitroanisole. Compounds, which were not further investigated, were formed with *l*-pinene, aniline, pyridine, β-naphthylamine, and numerous other substances.

Additive Products of 4′-Dimethylamino-2-methoxydistyryl Ketone.

m-*Dinitrobenzene.*—$C_{20}H_{21}O_2N,C_6H_4(NO_2)_2$, small, dull-red, prismatic needles, m. p. 78° (Found: N = 8·9. Calc., N = 8·85 per cent.).

s-*Trinitrobenzene.* — $C_{20}H_{21}O_2N,2C_6H_3(NO_2)_3$, reddish-purple needles with characteristic bronze reflex. M. p. 148° (Found: N = 13·5. Calc., N = 13·4 per cent.).

Fission of Substituted Styryl Methyl Ketones.

o-*Hydroxystyryl Methyl Ketone* (Harries, *Ber.*, 1891, **24**, 3180).—Four grams of the ketone, dissolved in 12·5 c.c. of absolute alcohol, were treated with 4 c.c. (2 mols.) of 50 per cent. sodium hydroxide solution. After two days 1·1 grams of the sodium salt of 2 : 2′-dihydroxydistyryl ketone were isolated. The salt was decomposed and the free ketone identified by its reactions and by the melting point after admixture of a specimen prepared according to Decker and Felser's method (*loc. cit.*).

p-*Dimethylaminostyryl Methyl Ketone.*—From this substance, proceeding in an analogous manner, *pp'*-tetramethyldiaminodistyryl ketone, m. p. 193°, was isolated; it was identified by the melting point of its mixture with a specimen prepared according to Sachs and Lewin (*Ber.*, 1902, **35**, 3576).

pp'-*Dimethoxydistyryl Ketone from* o-*Hydroxystyryl Methyl Ketone and Anisaldehyde.*—Four grams (1 mol.) of *o*-hydroxystyryl methyl ketone and 6·2 grams (2 mols.) of anisaldehyde, dissolved in the minimum quantity of absolute alcohol, were treated with 7 c.c. of a 50 per cent. solution of sodium hydroxide (3 mols.). After five days, 1·4 grams of almost colourless leaflets were filtered off and identified as the above compound by comparison and by the melting point of its mixture with a specimen obtained by Baeyer and Villiger's method (*Ber.*, 1902, **35**, 1191). It is interesting to note that, starting from *p*-methoxystyryl methyl ketone and salicylaldehyde, only resinous matter is produced. Similar results were obtained from *p*-methoxystyryl methyl ketone itself in presence of alkali.

pp'-*Tetramethyldiaminodistyryl Ketone from* o-*Hydroxystyryl Methyl Ketone and* p-*Dimethylaminobenzaldehyde.*—Sixteen grams of *o*-hydroxystyryl methyl ketone (1 mol.) and 15 grams of the aldehyde (1 mol.) were dissolved in 170 c.c. of absolute alcohol, and 80 c.c. of 10 per cent. aqueous sodium hydroxide (2 mols.) added. The mixture was kept for eight days at room temperature in cold weather. The red needles which had then separated were filtered off, and after crystallisation from alcohol–acetone mixture identified by the melting point and by analysis as *pp'*-tetramethyldiaminodistyryl ketone; the yield was 5 grams (Found : C = 78·5; H = 7·4; N = 8·7. Calc., C = 78·7; H = 7·5; N = 8·6 per cent.).

pp'-*Tetramethyldiaminodistyryl Ketone from the Additive Compound of 4'-Dimethylamino-2-hydroxydistyryl Ketone and* p-*Dimethylaminobenzaldehyde.*—A saturated alcoholic solution containing 4 grams of the additive compound was mixed with 2 c.c. of 50 per cent. sodium hydroxide. After six days, 1·5 grams of a mixture of *pp'*-tetramethyldiaminodistyryl ketone and a small quantity of the salicylaldehyde–sodium complex of the hydroxy-ketone were isolated.

Condensation of p-*Dimethylaminostyryl Methyl Ketone with Salicylaldehyde.*

This condensation was carried out in the hope of arriving at a more convenient method for the preparation of the hydroxy-ketone.

The reaction proved, however, to be very slow and was complicated by the slight solubility of the reactants. A considerable quantity of tar was invariably produced, from which only small quantities of the hydroxy-ketone melting at 154° were isolated, together with *pp'*-tetramethyldiaminodistyryl ketone.

In conclusion, we wish to express our appreciation of the interest taken in this work by Professor E. C. C. Baly, F.R.S., and to thank him for placing his spectrophotometer at our disposal. We also desire to acknowledge our indebtedness to the Advisory Council for Scientific and Industrial Research for a grant which has enabled this research to be undertaken.

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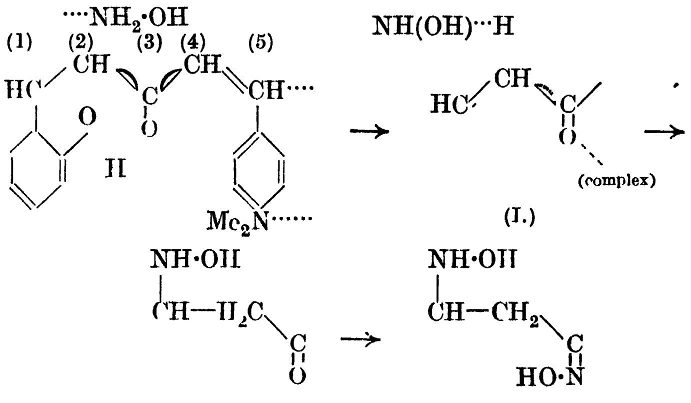
CLXXVIII.—*The Reactivity of Doubly-conjugated Unsaturated Ketones. Part II. The Action of Hydroxylamine, Semicarbazide, and Phenylhydrazine on 4'-Dimethylamino-2-hydroxydistyryl Ketone and its Methyl Ether.*

By ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK.

IT has been shown in the preceding paper that the high degree of reactivity exhibited by 4'-dimethylamino-2-hydroxydistyryl ketone may be satisfactorily explained by assuming inner complex formation involving the carbonyl oxygen atom and the hydroxyl group, the effect of this being to enhance the free residual affinity of the external carbon atom of the conjugated system included in the complex. In the present paper, further evidence is adduced strongly supporting this hypothesis.

Action of Hydroxylamine—By the action of hydroxylamine hydrochloride upon the hydroxy-ketone in presence of excess of calcium carbonate in the cold, a bright red, labile additive product (I), analogous to the solvates already described, can be isolated. This additive compound very readily loses its hydroxylamine addendum, with formation of the free ketone. If, however, more vigorous methods are employed, such as heating the reactants in concentrated alkaline solution for a short time, in place of the labile additive product, the true hydroxylamino-derivative (II) is produced in the form of almost colourless needles melting at 218°. Finally, an hydroxylamino-oxime (III) can be prepared by the action of hydroxylamine acetate on the ketone in the cold, but whereas the first two substances are rapidly prepared, this compound requires several days for its formation. With the methyl ether, on the other hand, only an hydroxylamino-oxime is produced. It is thus evident that the reaction takes place in successive stages, the first being labile addition by means of subsidiary valence linkings, followed by the strengthening of the partial linkings, finally resulting in the disruption of the double bond. Once this has taken place, the doubly conjugated system has ceased to exist, and, with it, the anomalous behaviour of the carbonyl group also vanishes, and consequently an oxime of the hydroxylamino-compound is obtained. It is likewise assumed that the reaction with hydroxylamine acetate follows the same course, as illustrated by the scheme:



(II). (III.)

Action of Semicarbazide.—The action of this base upon the hydroxyketone in presence of pyridine or of semicarbazide acetate itself results in the direct formation of a semicarbazido-semicarbazone, no intermediate compounds having been isolated. During the course of this investigation an interesting paper by Auwers has appeared (*Ber.*, 1921, **54**, [*B*], 987) in which it is pointed out that the conclusions arrived at by Rupe and his collaborators (*Ber.*, 1903, **36**, 1903; 1907, **40**, 4764), that it is only in the aliphatic group that semicarbazido-semicarbazones are obtainable, must be modified. Auwers, starting from phenyl propenyl ketone, *p*-anisyl propenyl ketone, and *p*-methoxy-*o*-tolyl propenyl ketone, readily obtained semicarbazido-semicarbazones, and concluded that whereas ketones of the type (A), probably owing to their spatial configuration, could only form semicarbazones, ketones of the type (B) examined by him, where the inhibiting influence of the phenyl group was removed, were not so restricted.

(A) $C_6H_5\cdot CH\colon CH\cdot COR$ (B) $C_6H_5\cdot CO\cdot CH\colon CHR$ (R = aliphatic group).

It is evident, however, from the above, that even compounds containing the ethylenic double bond adjacent to the phenyl group can, under certain conditions, react to yield semicarbazido-semicarbazones. Such a condition would be the strengthening of the necessary subsidiary valencies, which effect occurs, according to our postulate, in 4′-dimethylamino-2-hydroxydistyryl ketone. That, however, the addition of semicarbazide to an ethylenic linking under normal conditions takes place with more difficulty than the addition of hydroxylamine is illustrated by the action of 4′-dimethylamino-2-methoxydistyryl ketone, which only forms a simple semicarbazone. We regard this as a direct proof both of the presence of increased free valency on carbon atom C (1) and that the carbonyl group of the hydroxy-ketone remains inoperative until the complex partial valency system has been fundamentally altered by addition at the double bond.

Action of Phenylhydrazine.—A phenylhydrazone is obtained by the action of this base on either the hydroxy-ketone or its methyl ether. That, however, this is in no way contrary to the views just expressed is indicated by the fact that the reaction only takes place in presence of excess of pyridine, and that the phenylhydrazone contains, especially in the case of the hydroxy-ketone, one molecule of pyridine firmly attached. It is evident that the pyridine first forms a "solvate" with the ketone, analogous to the action of hydroxylamine in the formation of the hydroxylamine additive product, and that this occasions a rupture of the ring system, which then reacts to yield the phenylhydrazone–pyridine compound in the ordinary manner. Numerous experiments were carried out with the object of obtaining phenylhydrazine derivatives in the absence of pyridine, but without success, as oils which could not be purified invariably separated out. There can, however, be little doubt that such oils actually contained the phenylhydrazino-additive product analogous to the hydroxylamino-compound.

EXPERIMENTAL.

Additive Product of 4′-Dimethylamino-2-hydroxydistyryl Ketone with Hydroxylamine, $OH\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot CH\colon CH\cdot C_6H_4\cdot NMe_2,NH_2\cdot OH$.

2·8 Grams of the ketone (benzene additive product) were treated in alcoholic solution with 1·1 grams of an aqueous solution of hydroxylamine hydrochloride, and the mixture, after being neutralised with powdered calcium carbonate, was immediately filtered. On dilution with water, the additive product rapidly separated as bright scarlet flocks, from which the hydroxylamine addendum was easily removed by keeping over concentrated sulphuric acid (Found: on immediate analysis, N = 8·4. $C_{19}H_{19}O_2N,NH_2{\cdot}OH$ requires N = 8·6 per cent. Found: after two days in exsiccator, N = 4·7. $C_{19}H_{19}O_2N$ requires N = 4·8 per cent.).

Hydroxylamino-derivative of 4′-Dimethylamino-2-hydroxydistyryl Ketone.

8·4 Grams of the ketone–chloroform product, dissolved in 15·0 c.c. of 30 per cent. potassium hydroxide solution (4 mols.), were treated with 5·5 grams of hydroxylamine hydrochloride dissolved in 40 c.c. of water, and 20 c.c. of alcohol added to the mixture. The whole was boiled for a few minutes, when the solution changed colour, becoming orange-yellow. The hydroxylamino-compound rapidly separated and was purified by repeated crystallisation from absolute alcohol. It forms almost colourless needles, melting with decomposition at 218° (rapid heating). It is somewhat sparingly soluble in most organic solvents, and is slowly decomposed on boiling with hydrochloric acid or aqueous alkali (Found: C = 69·6; H = 6·9; N = 8·5. $C_{19}H_{22}O_3N_2$ requires C = 69·9; H = 6·8; N = 8·6 per cent.).

Hydroxylamino-derivative of 4′-Dimethylamino-2-hydroxydistyryl Ketoxime.

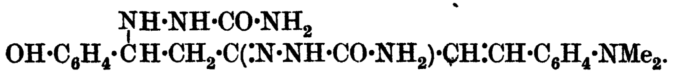
8·2 Grams of the ketone–chloroform product, dissolved in 50 c.c. of alcohol, were treated with 3 mols. of hydroxylamine acetate. The mixture was allowed to stand for three days, and the hydroxylamino-oxime precipitated by dilution with water. The dark tarry product was repeatedly crystallised from alcohol, after decoloration with animal charcoal. It forms pale yellow, silky leaves, which darken above 200° and finally melt with decomposition at 212° (Found: C = 66·7; H = 7·0; N = 12·3. $C_{19}H_{23}O_3N_3$ requires C = 66·9; H = 6·7; N = 12·3 per cent.).

Hydroxylamino-derivative of 4′-Dimethylamino-2-methoxydistyryl Ketoxime.

2·8 Grams of hydroxylamine hydrochloride (4 mols.), dissolved in the minimum quantity of water, were added to a solution of

3·1 grams of the methyl ether dissolved in 15 c.c. of pyridine. The mixture was kept for five days, and then diluted largely with water, when a yellow, oily mass was precipitated. After recrystallisation from a mixture of alcohol and pyridine, it was obtained in glistening, colourless needles melting at 214°. This compound may also be obtained by an analogous method to that employed in the preparation of the hydroxylamino-oxime of the hydroxyketone, a less favourable yield, however, being obtained (Found: $C = 67·3$; $H = 7·3$; $N = 11·9$. $C_{20}H_{25}O_3N_3$ requires $C = 67·6$; $H = 7·1$; $N = 11·8$ per cent.).

Semicarbazide Derivative of 4′-Dimethylamino-2-hydroxydistyryl Ketone Semicarbazone,



$$\overset{NH·NH·CO·NH_2}{OH·C_6H_4·CH}·CH_2·C(:N·NH·CO·NH_2)·CH:CH·C_6H_4·NMe_2.$$

4·0 Grams of the ketone (chloroform additive product), dissolved in 20 c.c. of pyridine, were mixed with 5·0 grams of semicarbazide hydrochloride dissolved in 15 c.c. of water, and 15 c.c. of alcohol were added in order to form a homogenous solution. After the mixture had been kept for two days, the flocculent, slightly red precipitate of the semicarbazide–semicarbazone was filtered off, and recrystallised from a mixture of aniline and amyl alcohol. It forms an almost colourless powder, melting at 218°, which is very sparingly soluble in most organic solvents, but is somewhat soluble in aqueous pyridine and readily soluble in warm aniline. This substance has also been prepared by the usual method with semicarbazide acetate (Found: $C = 59·0$; $H = 6·9$; $N = 22·8$. $C_{21}H_{27}O_3N_4$ requires $C = 59·3$; $H = 6·4$; $N = 23·1$ per cent.).

Semicarbazone of 4′-Dimethylamino-2-methoxydistyryl Ketone.

Three grams of an alcoholic solution of the methyl ether were mixed with an excess of semicarbazide acetate. After standing for two days, the precipitated semicarbazone was filtered off, and freed from unchanged methyl ether by washing with boiling alcohol. The semicarbazone, after recrystallisation from chloroform, forms brilliant yellow leaves melting at 213° (Found: $N = 15·3$. $C_{21}H_{24}O_2N_4$ requires $N = 15·4$ per cent.).

Pyridine Additive Product of 4′-Dimethylamino-2-hydroxydistyryl Ketone Phenylhydrazone.

16·4 Grams of the chloroform additive product of the ketone were dissolved in 50 c.c. of pyridine, and 17 grams (3 mols.) of phenylhydrazine hydrochloride added. The mixture was heated for thirty minutes on the water-bath, after which it was kept at the ordinary temperature. On cooling, the whole solidified to a yellow mass, which was redissolved in a small quantity of pyridine. Addition of ethyl acetate caused the separation of a small amount of a yellow substance readily soluble in water, but this was not further investigated. The ethyl acetate was driven off and the residue allowed to crystallise after the addition of alcohol. Ten grams of the hydrazone were thus obtained as a yellow, crystalline mass melting at 141°. On repeated crystallisation from benzene, the melting point gradually rises, which effect must be due to the gradual removal of the pyridine, as the substance melting at 141° can again be obtained by one recrystallisation from alcoholic pyridine. No accurate analytical results could be obtained for the compound of higher m. p., but it was indicated that the pyridine addendum was being partly replaced by benzene. None of the compounds gave the Knorr pyrazoline reaction (Found : $C = 78{\cdot}0$; $H = 6{\cdot}8$; $N = 12{\cdot}1$. $C_{25}H_{25}ON_3$ requires $C = 77{\cdot}9$; $H = 6{\cdot}5$; $N = 12{\cdot}2$ per cent.).

Phenylhydrazone of 4′-Dimethylamino-2-methoxydistyryl Ketone.

3·1 Grams of the methyl ether were dissolved in 15 c.c. of pyridine and treated with 4·3 grams (3 mols.) of phenylhydrazine hydrochloride. After heating for one hour on the water-bath, a pale yellow oil, which rapidly solidified on standing, separated out, and was recrystallised from alcohol–pyridine mixture. The phenylhydrazone forms pale yellow clusters, melting at 127°, readily soluble in pyridine, but only slightly soluble in alcohol. The results of analysis show this compound to be a pyridine additive product (Found : $C = 78{\cdot}0$; $H = 7{\cdot}0$. $C_{26}H_{27}ON_3,C_5H_5N$ requires $C = 78{\cdot}1$; $H = 6{\cdot}7$ per cent.). On recrystallising this compound from absolute alcohol, the pyridine is removed. The free phenylhydrazone consists of lemon-yellow prisms melting at 154°. This compound, as well as that obtained from the hydroxy-ketone itself, exhibits an intense greenish-yellow fluorescence in dilute solution (Found : $N = 10{\cdot}7$. $C_{26}H_{27}ON_3$ requires $N = 10{\cdot}6$ per cent.).

In conclusion, we desire to express our thanks to the Advisory Council for Scientific and Industrial Research for a grant which has enabled this investigation to be undertaken.

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CLXXIX.—*Surface Tensions of Salts of the Fatty Acids and their Mixtures.*

By Eric Everard Walker.

Those salts of the fatty acids which are useful soaps lower the surface tension of water to an altogether abnormal extent; a study of the surface tension of soap solutions is therefore of very special interest. The object of the present paper is to examine this property under a variety of conditions and thereby to learn something of the changes which take place in solution when the temperature or concentration is varied or when one soap is wholly or partly replaced by another of the same or a nearly related series.

It was believed that the information so gained would lead to a better understanding of the manner in which different soaps interact in solution to produce an effect on the surface tension which is either greater or less than would be expected from the proportions in which the constituents are present.

The results have to a large extent justified expectations, in that a theory primarily advanced in order to explain the manner in which surface tension varies with temperature, concentration, and the number of carbon atoms, has been found capable of explaining the behaviour of mixed soaps in solution.

Measurement of Surface Tension.

The surface tension was measured with a simple form of dropping pipette. It is not claimed that the results obtained are of absolute value, and in fact it was found that different pipettes gave different results. It is, however, well known that the apparent surface tension of soap solutions depends to a very marked extent on the exact conditions under which it is determined. All that can be claimed is that the conditions were carefully standardised so that the results might be of comparative value. The pipette and receiver were completely immersed in a constant-temperature bath, necessitating a simple device outside the water-bath for regulating the rate of flow. This consisted of a U-tube connected with the upper end of the pipette and fitted with a tap on the longer arm. Water was allowed to flow from the longer arm into the shorter at a regulated speed, thus allowing the soap solution to flow out of the pipette at a similar rate.

The required quantity of acid was weighed out, dissolved in alcohol, and neutralised with an alcoholic solution of sodium hydroxide. This was evaporated, the residue dissolved in water and the solution made up to the required weight. The water used was redistilled and the first and last thirds were rejected. The alcoholic sodium hydroxide solution was made up by dissolving sodium in alcohol redistilled over lime. All concentrations were expressed in terms of the number of grams of *acid* per 100 grams of solution.

Solutions made up in this way could be kept unchanged for a day or so. If the alcoholic sodium hydroxide solution is made up with ordinary stick sodium hydroxide, progressive rise in the surface tension takes place, noticeable after an hour or so. The effect of keeping solutions made as described is shown in the following table.

Surface Tension in dynes per cm.

	Laurate.	Myristate.	Palmitate.
Fresh solution	29·2	19·8	19·8
After four hours at 60°	29·2	19·7	19·8
After twenty-four hours at 60°	29·1	19·5	19·9
After eight days at room temperature	29·9	19·7	20·2

The soap solution, which had been kept at the required temperature for fifteen minutes or longer, was drawn up into the pipette, taking care to avoid air bubbles. The regulating U-tube and the receiver were then attached and the apparatus was placed in the water-bath. Five minutes were allowed to elapse before the determination was made, in order that the temperature might become uniform.

The soap solution was then adjusted to the top mark on the pipette, approximately 2 c.c. were run out drop by drop at a rate of 20 drops every minute, the flow being stopped at the first complete drop after the 2 c.c. mark had been passed. The pipette was calibrated to read to 0·01 c.c. between 2·0 c.c. and 2·1 c.c. The volume was then reduced to grams for the purpose of calculation.

Twenty drops every minute was chosen as the rate of flow. A much slower rate has its advantages, especially in the case of soap solutions, but it was considered unsatisfactory in the present instance on account of the tendency of moisture to condense on the jet and drop at high temperatures, and of the probability that unsaturated soaps would interact with the atmosphere.

All surface tensions were calculated with reference to the drop number of water determined with the same pipette, at the same temperature as that used for the determination of the soap solution.

Effect of Concentration.

In this manner the surface tensions of several salts of the fatty acids were determined at concentrations varying from 0·005 per

TABLE I.

Surface Tension at 60° in dynes per cm.

Concentration.	Laurate.	Myristate.	Palmitate.	Stearate (impure).	Arachidate.	Oleate.
0·005	64·0	64·0	64·2	65·7	—	65·7
0·01	61·3	54·7	42·2	52·0	—	46·9
0·025	54·9	39·2	26·6	32·5	—	28·0
0·05	45·9	26·9	21·85	26·7	65·3	23·75
0·075	41·1	22·5	20·95	24·4	—	22·95
0·1	38·0	21·2	20·5	23·9	61·0	22·55
0·15	—	20·3	19·95	—	—	—
0·2	29·2	20·6	19·85	22·4	56·9	—
0·25	—	21·2	—	—	—	—
0·3	24·5	—	20·7	22·5	—	—
0·4	—	23·9	22·3	—	56·7	—
0·5	21·2	—	—	23·1	—	—
0·75	26·5	—	—	23·1	—	—
1·0	28·3	26·4	23·65	23·6	—	—
1·5	29·3	—	—	—	—	—
2·0	29·4	—	—	—	—	—

cent. to 1·0 per cent. The standard temperature chosen was 60°. The results (mean values) are given in Table I. In Fig. 1 these results are represented graphically. The concentration is represented by the abscissæ and the *lowering of the surface tension* (water = 66·0 dynes/cm. at 60°) by the ordinates.

The palmitic acid was impure. It had the correct equivalent, but contained about 7 per cent. of oleic acid and melted at 58—59°. The stearic acid was a commercial sample. It contained only 1·5 per cent. of oleic acid, but about 40 per cent. of palmitic acid. It was, however, suited to the present purpose, since the pure soap is only soluble to the extent of 0·2 per cent. at 60°. The remaining acids were practically pure. With the exception of "stearic acid," however, they all give a good idea of the general trend of the curve. It is interesting to note that this impure soap follows closely the contour of the palmitate curve, although it contains a preponderating proportion of stearate. This will be referred to later in the section on mixtures. The interesting point about these curves is that they tend to rise to a maximum and that this maximum is almost the same for all soaps the solubility of which is great enough to allow the maximum to be reached. This is very suggestive, and indicates that at this point the surface layer of all soaps is similar. Probably it consists of a stable emulsion containing a high percentage of soap.

Using carefully purified materials, the initial part of the curve was redetermined. Special care was taken over these determinations, since it is at these low concentrations that different soaps can best be compared with one another. For instance, it is scarcely fair to compare a 0·2 per cent. palmitate solution with a 0·2 per cent. laurate solution, since the former has reached its maximum while the latter has not. At a concentration of 0·5 per cent., sodium laurate would appear to be more effective than either myristate or palmitate. As the tip of the pipette had been damaged, it was necessary to use a new one, and as this gave different results from the old one, the results are not directly comparable. Two completely independent series of measurements were made, except in the case of sodium arachidate, and the mean values are given in Table II.

Fig. 1.

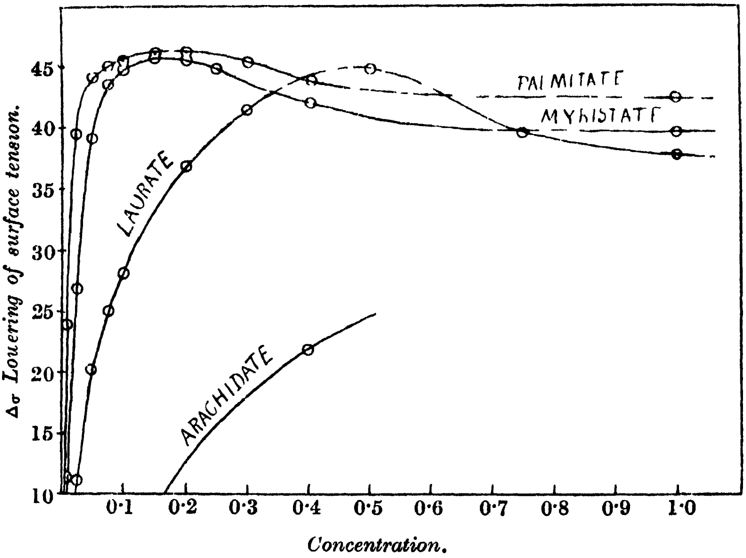


TABLE II.

Lowering of Surface Tension at 60° in dynes per cm.

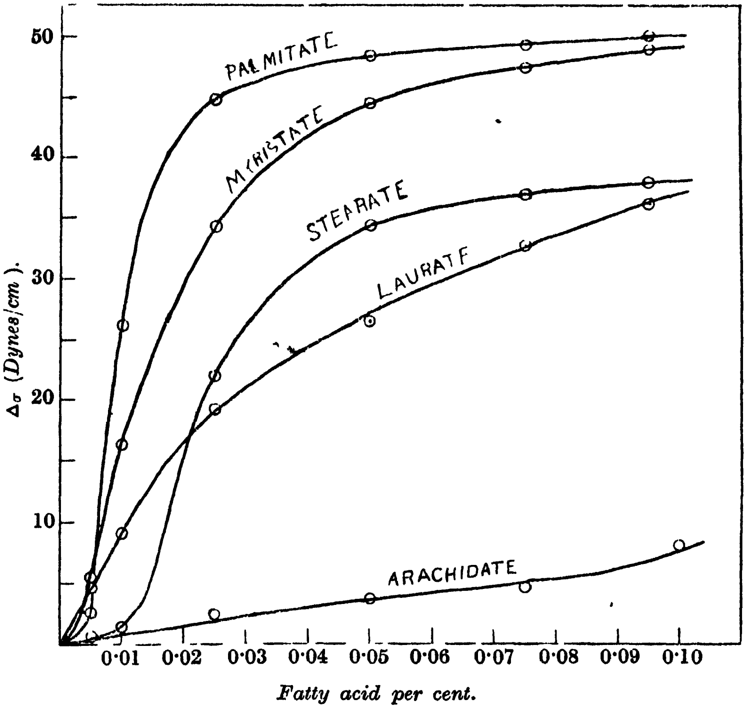
Water—66·0. Pipette No. 3.

Concentration.	*n*-Octoate.	*n*-Decoate.	Laurate.	Myristate.	Palmitate.	Stearate.	Arachidate.*	Behenate.
0·005	—	—	4·7	5·4	2·5	0·6	—	—
0·01	—	—	9·1	16·3	26·1	1·3	—	—
0·025	—	—	19·3	34·3	44·8	22·0	2·3	—
0·05	—	—	26·7	44·6	48·4	34·4	3·6	—
0·075	—	—	32·8	47·5	49·3	36·9	4·6	—
0·1	1·55	6·4	36·2	48·9	50·0	37·7	8·1	1·6

* Single series of determinations only.

Curves are plotted in Fig. 2. The interesting part about these curves is the first inflection in the early part of the curve, and the significance of this will be considered in the section on theory. It should be pointed out that sodium stearate does not form a clear 0·1 per cent. solution like sodium myristate and laurate; the solution has at 60° a curious opalescent appearance, due, no doubt, to the presence of colloidal particles. Bearing in mind McBain's work on the proportions in which colloidal soap is present in solution, it seems probable that this phenomenon may be due to partial hydrolysis.

FIG 2.



Effect of Temperature.

The temperature coefficients of the surface tensions of pure liquids have led to results of great theoretical significance. In the case of solutions and mixtures, however, conditions are much more complex and theory has not made much headway.

Fig. 3 illustrates forcibly the effect of temperature in the case of sodium arachidate. At 60°, it lowers the surface tension only to a very small extent; at 90°, however, the whole contour of the curve is altered and becomes similar to that of sodium stearate at 60°.

The full line in the 60° curve represents the behaviour of a perfectly fresh solution. The dotted line indicates the surface tension of a solution which has been kept at a temperature of 60° for some time and has partly gelatinised.

Fig. 3.

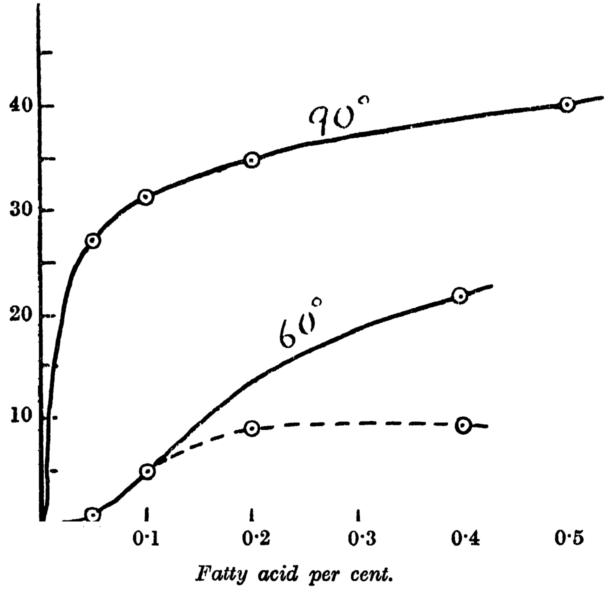


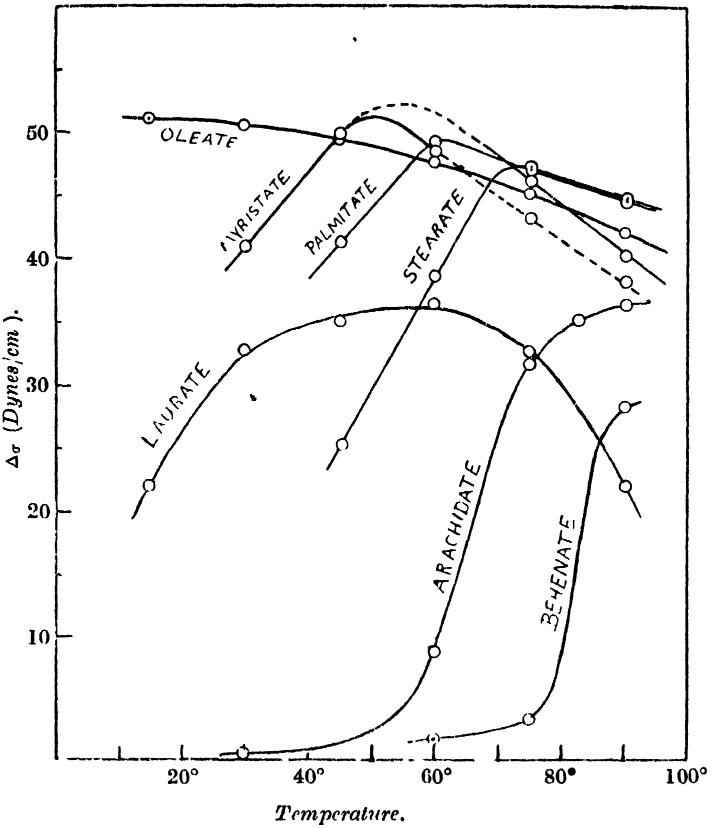
TABLE III.

Temperature Curves.—Pipette No. 3.

Temp.	Oleate. 0·1%	Laurate. 0·5%	Laurate. 0·1%	Myristate. 0·1%		Palmitate. 0·1%	Stearate. 0·1%	Arachidate. 0·1%	Behenate. 0·1%
15°	51·1	51·8	22·0	—		—	—	—	—
30	50·58	51·55	32·75	41·0		—	—	0·5	—
45	49·4	49·65	35·15	50·0		41·3	25·2	—	—
60	47·7	48·0	36·45	48·5		49·3	38·7	8·6	1·6
75	45·15	45·75	32·75	46·25	(43·25)	47·0	47·2	31·6	3·15
90	42·1	41·9	21·9	40·2	(38·2)	44·4	44·6	36·3	28·2
							T=82·7°	35·1	

In Table III data obtained at various temperatures are recorded, and curves are plotted in Fig. 4. In general, the extent to which the surface tension is lowered increases to a maximum with the temperature, and then decreases. Sodium oleate either shows no maximum or more probably it is below 15°. In most cases, the temperature at which the maximum occurs rises with the molecular weight, but the behaviour of sodium laurate is exceptional. At a higher concentration (0·5 per cent.), however, the laurate curve becomes almost identical with the 0·1 per cent. oleate curve, and thus falls more or less into its place. Sodium oleate itself is interesting, and differs from all the other soaps at 0·1 per cent. concentration in that its efficiency in lowering the surface tension remains high over a wide range of temperature.

Fig 4



Effect of Molecular Weight.

The manner in which the effect of the salts of the fatty acids on the surface tension of water changes from member to member

TABLE IV.

Palmitate and Myristate 60°.

% Palmitate.	$\Delta\sigma$.	Deviation.
0	48·95	—
25	49·15	−0·1
50	49·5	+0·1
75	49·6	−0·05
100	49·9	—

Palmitate and Stearate 60°.

% Palmitate.	$\Delta\sigma$.	Deviation.
0	39·15	—
25	43·75	+1·9
50	46·0	+1·5
75	48·25	+1·05
100	49·9	—

Oleate and Stearate 60°.

% Oleate.	$\Delta\sigma$.	Deviation.
0	38·35	—
25	46·9	+6·2
50	48·05	+5·05
75	48·3	+3·0
100	47·65	—

Palmitate and Oleate 60°.

% Palmitate.	$\Delta\sigma$.	Deviation.
0	47·75	—
25	48·25	+0·1
50	49·1	0·15
75	49·55	=0·0
100	50·15	—

Myristate and Laurate 60°.

% Myristate.	$\Delta\sigma$.	Deviation.
0	33·4	—
25	43·9	+5·7
50	46·35	−5·3
75	47·85	+3·05
100	48·6	—

Arachidate and Laurate 60°.

% Arachidate.	$\Delta\sigma$.	Deviation.
0	34·3	—
25	9·6	−18·3
50	9·3	−12·15
75	9·0	−6·0
100	8·6	—

Oleate and Myristate 60°.

% Oleate.	$\Delta\sigma$.	Deviation.
0	48·7	—
25	47·75	−0·3
50	47·6	−0·6
75	47·65	−0·3
100	47·7	—

Stearate and Arachidate 60°.

% Stearate.	$\Delta\sigma$.	Deviation.
0	7·4	—
25	25·4	+10·0
50	34·2	−10·8
75	38·15	+6·7
100	39·45	—

Palmitate and Myristate 45°.

% Palmitate.	$\Delta\sigma$.	Deviation.
0	50·3	—
25	44·75	−2·75
50	42·25	−2·55
75	40·85	−1·3
100	39·35	—

Stearate and Laurate 60°.

% Stearate.	$\Delta\sigma$.	Deviation.
0	34·6	—
25	29·3	−7·2
50	30·3	−5·8
75	35·0	−1·8
100	37·55	—

Oleate and Laurate 60°.

% Oleate.	$\Delta\sigma$.	Deviation.
0	37·0	—
25	45·55	+5·85
50	46·75	+4·35
75	47·4	+2·35
100	47·75	—

n-Decoate and *n*-Octoate 60°.

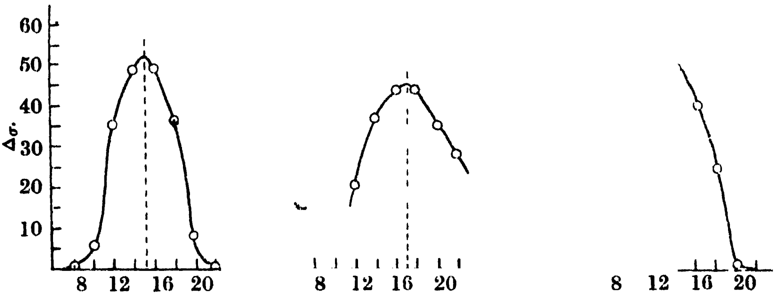
% Decoate.	$\Delta\sigma$.	Deviation.
0	1·55	—
25	2·2	−0·6
50	4·7	+0·7
75	13·6	+8·4
100	6·4	—

of the series is remarkable when we consider the gradual way in which most properties change as an homologous series is ascended. Just as in the case of temperature and concentration, the activity of the soap rises to a maximum, after which an increase in the molecular weight is associated with a decrease in the activity of the soap. The curves in Fig. 5 show how the effect on the surface tension varies with the number of carbon atoms under various conditions.

Mixed Soaps.

Solutions of 0·1 per cent. strength were made up as usual and the surface tension of these was determined. The solutions were then mixed in various proportions and the surface tension of the mixtures determined. The results are recorded in Table IV. In Fig. 6 the results are represented diagrammatically by plotting the deviations from the "mixture law" against the composition of the solution. If a series of mixtures follows the "mixture law," that is, the surface tension of all mixtures is equal to the weighted mean of that of the constituents, the curve then becomes a horizontal straight line as in the case of palmitate and myristate or palmitate and oleate. The majority of mixtures are, however, represented by curves falling either above or below this hypothetical line.

Fig. 5.

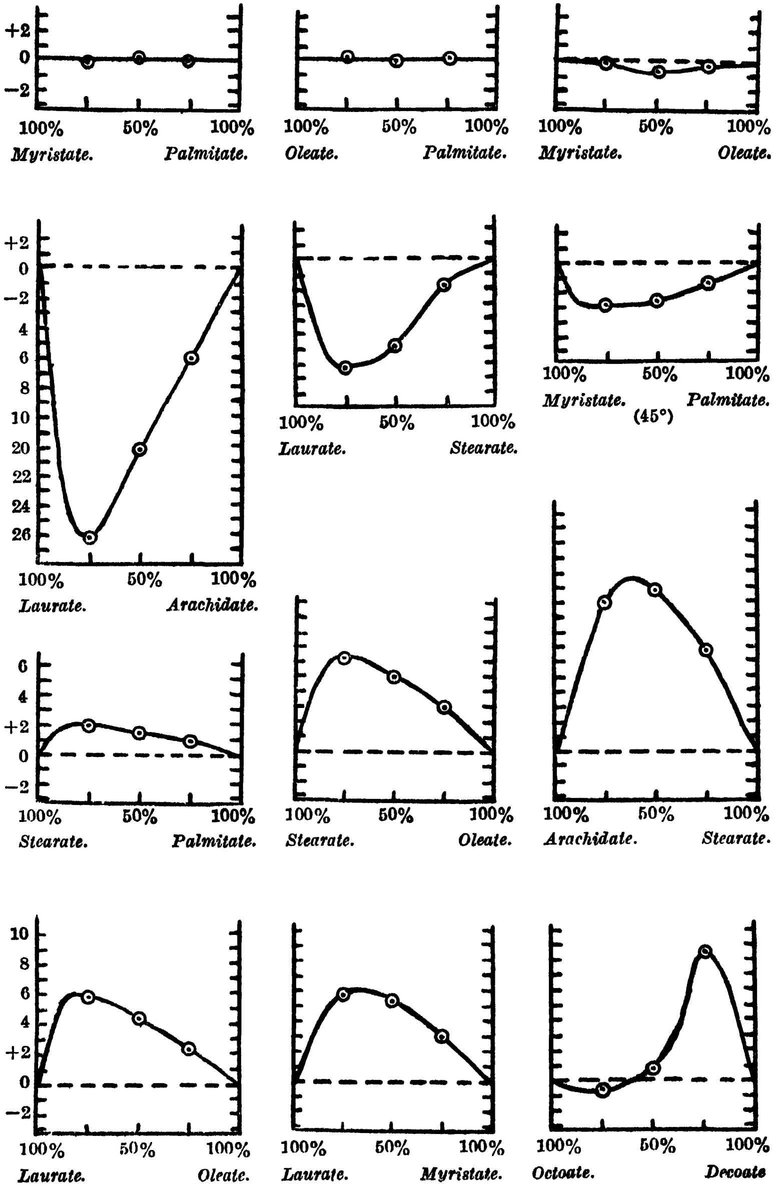


Number of carbon atoms in the fatty acid.

Theoretical.

It has been shown that molecular weight, temperature, and concentration all exert an effect on capillary activity which rises to a maximum and then decreases. From this it would appear that there must be some condition of equilibrium between two forms of soap present in solution, and that if this equilibrium is disturbed, either *in one direction or the other*, by changes in temperature or

Fig. 6.


+2
0
−2
100% 50% 100%
Myristate. *Palmitate.*
100% 50% 100%
Oleate. *Palmitate.*
100% 50% 100%
Myristate. *Oleate.*
+2
0
−2
4
6
8
10
20
22
24
26
100% 50% 100%
Laurate. *Arachidate.*
100% 50% 100%
Laurate. *Stearate.*
100% 50% 100%
Myristate. *Palmitate.*
(45°)
6
4
+2
0
−2
100% 50% 100%
Stearate. *Palmitate.*
100% 50% 100%
Stearate. *Oleate.*
100% 50% 100%
Arachidate. *Stearate.*
10
8
6
4
+2
0
−2
100% 50% 100%
Laurate. *Oleate.*
100% 50% 100%
Laurate. *Myristate.*
100% 50% 100%
Octoate. *Decoate*

concentration (or by substituting another soap of greater or smaller molecular weight), the property of lowering the surface tension (or interfacial tension) will be greatly diminished or will disappear.

These facts can be explained and a foundation for the theory of soap mixtures laid if we regard soap in aqueous solution as containing colloidal aggregates or "micelle" in equilibrium with simpler molecules. This view has long been advocated by McBain, who arrived at this conclusion in order to explain the osmotic behaviour of soap solutions in relation to their electrical conductivity.

It may be assumed with reason that the equilibrium between these colloidal aggregates and the simpler molecules is affected by temperature and concentration in much the same manner as is the equilibrium between complex and simple molecules.

Thus dissociation is promoted by :—

increase in temperature,
decrease in molecular weight,
decrease in concentration;

and association is promoted by :—

decrease in temperature,
increase in molecular weight,
increase in concentration.

It should be remembered that on account of the lowering of the surface tension the solution is more concentrated in the surface layer. In the case of those soaps lowering the surface tension to a large extent, there must be some circumstance which facilitates the concentration of the soap in the surface layer. This is to be found in the readiness with which they form complex colloidal molecules. According to McBain, there are only immeasurably small quantities of colloidal soap in dilute solutions. At the surface, however, under the influence of high concentration and high pressure, conditions are suitable for the formation of large colloidal aggregates. The lowering of the surface tension tends to hold these at the surface against their osmotic pressure. This osmotic pressure is, however, small and the surface concentration is therefore abnormally great.

To bring this theory into line with facts, we must assume that very large micelle are not so active, weight for weight, in lowering the surface tension of soap solutions as those of moderate size. Therefore, if the size of the colloidal aggregates is increased beyond a certain limit, there is a falling off of efficiency, even although the surface concentration may remain high. Such an assumption is reasonable in view of the fact that the special forces active in the surface layer only penetrate beneath the surface to an extent depending on the range of molecular action (see Parks, *Phil. Mag.*, 1903, [vi], 5, 517). Therefore, when the colloidal particles reach dimensions which are large in comparison with molecular magnitudes, a falling off in efficiency must necessarily be expected (Lewis claims that emulsions of paraffin in aqueous solution have little or no effect on the interfacial tension. *Phil. Mag.*, 1908, [vi], **15**, 499). Hence we have the following system :—

Small micelle efficient in lowering the surface tension, but difficult to chain to the surface on account of their relatively high osmotic pressure.	Large micelle inefficient in lowering the surface tension, but easy to chain to the surface on account of their relatively low osmotic pressure.

It may be assumed that the highly efficient soaps, such as palmitate and myristate, are those in which surface concentration and specific activity are so combined as to give a maximum value. Those of lower molecular weight are less efficient because the relatively high osmotic pressure of the small micelle hinders the formation of a high surface concentration. The higher homologues readily form large micelle, which, having a low osmotic pressure, are easily adsorbed in the surface layer. Nevertheless, one would expect that the surface concentration of stearate, arachidate, and behenate would be progressively less than that of palmitate on account of the decreased activity of the larger micelle. There is, however, every reason to suppose that the surface concentration of these soaps is much greater than that of the "nut oil" soaps, which lower the surface tension to a corresponding extent (see p. 1522).

Milner (*Phil. Mag.*, 1907, [vi], **13**, 96) and Lewis (*Phil. Mag.*, 1908, [vi], **15**, 499; 1909, [vi], **17**, 466) examined the relationship between surface tension and surface concentration for a variety of solutions in the light of Gibb's theory. Both authors grafted on to this theory the assumption that the solutions with which they were dealing followed the gas laws, and found that the majority of substances were very much more concentrated in the surface layer than the theory thus modified would lead them to expect. Lewis found that Congo-red was about thirty times and sodium oleate about one hundred times more concentrated in the surface layer than the theory required. McBain's work has proved that the gas laws cannot be applied to such substances in concentrated solution, and their theory was not therefore applicable to these cases, for the concentration is high in the surface layer, even although small in the body of the solution. Lewis explained the apparent discrepancy by assuming that gelatinisation takes place in the surface layer. No special hypothesis is required, however, if McBain's theory of colloidal electrolytes is accepted.

(a) *Relationship between Surface Tension and Concentration.*

When the soap solution is extremely dilute, the concentration in the surface layer will be sufficiently small for the soap to consist mainly of simple molecules. As the concentration is increased, complexes will increase in the surface layer, slowly at first and then with increasing rapidity. The more complexes are formed the smaller will be the work required to be done by surface tension against the osmotic pressure in order to concentrate the soap in the surface layer.

McBain's work has shown that the osmotic pressure rises fairly rapidly with the concentration until a maximum is reached, and that it then falls slightly, thereafter rising much more slowly. As soon as the point is reached at which an increase in concentration is associated with an actual decrease in osmotic pressure, followed by a region in which the osmotic pressure rises slowly with the concentration, a very rapid increase in the surface concentration must necessarily follow. One would therefore expect that the surface concentration would at first increase slowly with the volume concentration and then with increasing rapidity.

These expectations are realised in the early part of the concentration curves (see Fig. 2), and, moreover, this first inflection becomes more marked as the molecular weight (and therefore the tendency to form complexes) increases.

The occurrence of a maximum in the surface-tension curve is explained by the hypothesis that the efficiency of the colloid particles falls off as their size increases, hence the whole form of the concentration curve is in qualitative agreement with the requirements of theory.

The form of McBain's concentration–osmotic pressure curves shows that there are in certain circumstances three concentrations having one and the same osmotic pressure.

Since surface tension is so intimately connected with osmotic pressure, it would not be surprising to find that for one and the same volume concentration there could be more than one surface tension. This appears to be the case for sodium myristate at 75° and 90°. The readings were as follows :—

	Drops per gram.		Drops per gram.
75°	112	90°	84·5
	111·5		84
	94·5		101
	96·5		105
	113		103
	112		103

In another series of five readings for a temperature of 75° and using another pipette, only one high reading was obtained.

Attempts to obtain either the one reading or the other by approaching the temperature from above or below met with no success. The phenomenon is therefore different from that observed in the case of arachidic acid. Moreover, gelatinisation was not observed and would not be expected at this temperature.

(*b*) *Temperature.*

The theory is in harmony with the fact that there is an optimum temperature for every soap and that in general this rises as the homologous series is ascended. This optimum temperature appears to have some connexion with the melting point of the acid. It seems not unreasonable to suppose that at the melting points of the acids, the corresponding soaps exist in approximately similar molecular states so far as their tendency to form complexes is concerned.

(*c*) *Mixed Soaps.*

There are three ways in which mixed soaps might be expected to behave in dilute solution.

(1) The soaps might act independently, each constituent lowering the surface tension to an extent corresponding with its individual concentration. In this case, owing to the form of the concentration curves, almost any mixture would be much more efficient than a single soap, weight for weight. Mixtures would not be expected to behave in this way unless they were very dilute both in solution and *in the surface layer.* It would not, therefore, be in accordance with the theory, and is not, in fact, found to be the case.

(2) The soaps might form mixed complexes at the surface having properties intermediate between those of the constituents. If these mixed complexes in the surface layer contained the constituents in the same proportions in which they were present in solution, one might expect that the resultant lowering of the surface tension would be approximately the weighted mean of those of the constituents at the combined concentration of the mixed soaps, that is, the mixed soaps would apparently follow the so-called mixture law. There is, however, no reason to suppose that two different soaps would be adsorbed to the same extent in the surface layer either in the form of mixed complexes or otherwise. Hence it is only in the case of mixtures of soaps lowering the surface tension to approximately the same extent that one would expect the mixture law to be followed.

Thus, for instance, the three pairs :—

Myristate and palmitate at 60°.
Oleate and myristate ,, ,,
Oleate and palmitate ,, ,,

follow very closely the mixture law (see Fig. 6). At 45°, however, palmitate lowers the surface tension to a much smaller extent than myristate. Accordingly, at this temperature the mixture law is not followed. Laurate and stearate also lower the surface tension to about the same extent; they are, however, very dissimilar in other respects, the form of the concentration curves being very different. Mixtures of these two soaps do not follow the mixture law. It is, therefore, reasonable to suppose that in these circumstances the complexes formed do not possess properties intermediate between those of the two constituents.

(3) The majority of soap mixtures come under the third head, the capillary activity of the mixtures being related in no simple manner to that of the constituents. Having shown that the mixture law holds fairly closely under certain conditions, the simplest plan is to regard all mixtures not following this law as lowering the surface tension by so much more or so much less than the law would indicate. The behaviour of mixtures is therefore represented graphically on this plan in Fig. 6. From what has been said in the preceding paragraph one would expect that that soap which is most readily absorbed in the surface layer would have the predominant effect; in what follows such a soap will be called a dominant soap. As a general rule this soap will be the one which lowers the surface tension to the largest extent. This is not, however, necessarily the case, since the lowering of the surface tension depends on *two factors* :—

(1) Concentration in the surface layer.
(2) Specific activity of the soap in the surface layer.

If the dominant soap lowers the surface tension more than the other, mixtures of the two will have a *lower* surface tension than the mixture law would indicate. If, on the other hand, the dominant soap lowers the surface tension to a smaller extent than that with which it is mixed, the reverse is to be expected. All the mixtures hitherto examined, with the exception of laurate and stearate, conform to this rule if the soaps are regarded as dominating each other in the order of the following empirical list :—

1. $\left\{\begin{array}{l}\text{Palmitate–}C_{16}\\ \text{Oleate}\end{array}\right.$
2. Stearate–C_{18}
3. Arachidate–C_{20}
4. Behenate–C_{22}
5. Myristate–C_{14}
6. Laurate–C_{12}
7. *n*-Decoate–C_{10}
8. *n*-Octoate–C_8

This list, although empirical in a sense, is nevertheless in harmony with the theory put forward in this paper, which requires that the adsorptive powers (or the tendency of the soap to concentrate at the surface) shall increase to a maximum as the homologous series is ascended and then decrease. A very interesting example of the way in which one soap can almost completely dominate another in the surface layer is the case of laurate and arachidate. Arachidate lowers the surface tension by 8·6 dynes, and laurate by 34·3 dynes, nevertheless, when 75 per cent. of the arachidate is replaced by laurate the extent to which the mixture lowers the surface tension is only increased to 9·6 dynes. With regard to the form of the curves in Fig. 6, theory indicates that the greatest deviation from the mixture law should occur when a small quantity of the dominant soap is mixed with a large quantity of the other, that is, the peak of the curve should always be displaced towards that end of the diagram corresponding with low concentrations of the dominant soap. This is so in nearly every case investigated, even in the somewhat exceptional case of laurate and stearate. Mixtures of decoate and octoate are the only exceptions in this respect.

The exceptional behaviour of mixtures of laurate and stearate indicates that the principles enunciated cannot be applied absolutely rigidly. They cover perhaps the most important aspect of the problem, but when the difference in the adsorptive power is large and the difference between the capillary activities is small, as in the case of this pair, then these effects may be masked by secondary changes. Evidence of such changes is also found in the case of mixtures of oleate and stearate, and decoate and octoate, where certain mixtures lower the surface tension to a *greater* extent than either of the constituents.

Summary of Results.

The activity of various salts of the fatty acids in lowering the surface tension of water has been examined at various concentrations and temperatures, and the manner in which this activity varies with changing conditions has been explained on the basis of McBain's theory of soap solutions.

Only one additional hypothesis has been found to be necessary, and this is to the effect that the lowering of the surface tension is not solely proportional to the concentration in the surface layer, but that it depends also on the size of the colloidal particles. McBain's theory, together with this hypothesis, suffices to explain the following facts.

(1) Soaps lower the surface tension of the water in which they are dissolved to an altogether abnormal extent.

(2) In an homologous series of soaps the power of lowering the surface tension first rises with increasing molecular weight and then falls after passing through a maximum.

(3) In general, the property of lowering the surface tension rises to a maximum as the temperature is increased and then falls off.

(4) The property of lowering the surface tension increases slowly with the concentration at extreme dilution, then rises rapidly and after passing through a maximum decreases again.

(5) When soaps are mixed in solution, the extent to which they lower the surface tension cannot be determined from the properties of the constituents. By means of the theory it is possible, as a rule, to determine whether a mixture of any two soaps will lower the surface tension more or less than the weighted mean of the constituents.

In conclusion, the author desires to acknowledge the permission of Messrs. Joseph Crosfield and Sons, Ltd., to publish this paper.

KIRHI,
INDIA.

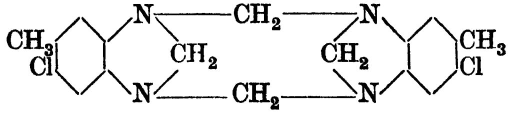
[*Received, May* 12*th*, 1921.]

CLXXX.—ortho-*Chlorodinitrotoluenes. Part III. Bases derived from 2-Chloro-4 : 5-dinitrotoluene.*

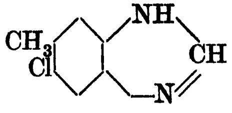
By GILBERT T. MORGAN and WILLIAM ARTHUR PERCIVAL CHALLENOR.

2-CHLORO-4 : 5-DINITROTOLUENE, described in Part I of this communication (T., 1920, **117**, 786), gives rise to 6-chloro-3 : 4-tolylenediamine, an exceptionally stable *ortho*-diamine, which, when starting from *o*-toluidine, can be prepared by methods giving an overall yield of about 33 per cent. On this account the base can with advantage be substituted for *o*-phenylenediamine in those condensations where a diamine is employed in the characterisation of α-diketones or *ortho*-quinones. With these dicarbonyl compounds the new diamine gives rise to well-defined, readily crystallisable derivatives.

As an example of condensation with monocarbonyl derivatives, the interactions of 6-chloro-3 : 4-tolylenediamine and formaldehyde were examined in neutral and in acid solutions. Under the former of these conditions two dimeric hydrolysable condensation products were obtained, each of which had the composition corresponding with *tetramethylene*bis-6-*chloro*-3 : 4-*tolylenediamine*. The possibility of isomerism is indicated by the following formulæ I and Iᴀ.



(I.)



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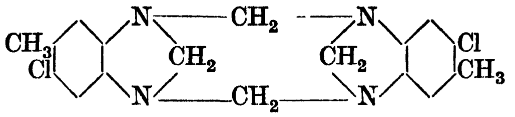
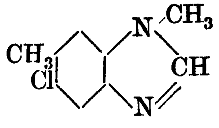


(Iᴀ.)



(III.)

In acid solution, the formaldehyde condensation takes a different course, the monomeric non-hydrolysable 5-*chloro*-1 : 6-*dimethylbenziminazole* (III) being produced. This amidine is also obtained by condensing 6-*chloro*-3N-*methyl*-3 : 4-*tolylenediamine* with formic acid, an alternative method of preparation which demonstrates its constitution.

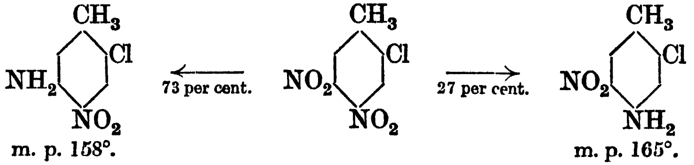
The amidine condensation proceeds normally also with 6-chloro-3 : 4-tolylenediamine and its 3*N*-phenyl derivative, the constitution of the resulting methenyl compounds being represented respectively by formulæ II and VI.

Action of Ammonia on 2-*Chloro*-4 : 5-*dinitrotoluene. A Correction.*

Attention has been directed in Part I of this communication (T., 1920, **117**, footnote, p. 789) to a discrepancy in the melting points of two different preparations of 6-chloro-4-nitro-*m*-toluidine. The product obtained by the action of alcoholic ammonia on 2-chloro-4 : 5-dinitrotoluene melted at 144°, whereas the substance previously obtained by nitrating 6-chloro-aceto-*m*-toluidide melted at 158—159° (B.A.S.F., D.R.-P. 226772).

It has now been found that the more fusible product is a mixture of approximately 73 per cent. of 6-chloro-4-nitro-*m*-toluidine and 27 per cent. of 6-chloro-3-nitro-*p*-toluidine (m. p. 165°). This mixture retains its composition on repeated crystallisation from alcohol, petroleum (b. p. 80—90°), or glacial acetic acid, and has the appearance of being a homogeneous substance. A similar difficultly separable mixture of dinitrotoluidines has been observed by Körner and Contardi (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339).

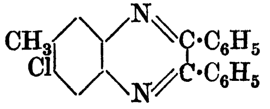
This observation is of some theoretical interest as illustrating Kenner's theory of the replacement of nitro-groups by amino-radicles (T., 1914, **105**, 2717; 1920, **117**, 852). In the present instance the two nitro-groups are alternatively removed in the following proportions.



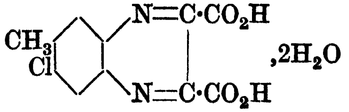
EXPERIMENTAL.

6-Chloro-3 : 4-tolylenediamine was readily prepared by the following series of reactions. Redistilled *o*-toluidine, nitrated in concentrated sulphuric acid, gave a mixture of 4- and 6-nitro-*o*-toluidines, which was separated by fractional crystallisation of the hydrochlorides; the yield of 4-nitro-*o*-toluidine was 75 per cent., whilst about 2—5 per cent. of the 6-nitro-isomeride was isolated from the more soluble fraction (Noelting and Collin, *Ber.*, 1884, **17**, 265; Green and Lawson, T., 1891, **59**, 1013). Application of the Sandmeyer reaction to the chief product gave an 80 per cent. yield of 2-chloro-4-nitrotoluene. Nitration of the chloro-derivative furnished 2-chloro-4 : 5-dinitrotoluene (85 per cent.) and upwards of 4 per cent. of 2-chloro-4 : 6-dinitrotoluene. The dinitro-compound was converted quantitatively into crude 6-chloro-4-nitro-*m*-toluidine (yield 97 per cent.) by alcoholic ammonia and this base reduced to 6-chloro-3 : 4-tolylenediamine (yield 85 per cent.) with zinc dust and dilute alcohol containing ammonium chloride (T., 1920, **117**, 786).

Condensation of 6-*Chloro*-3 : 4-*tolylenediamine with α-Diketones and* ortho-*Quinones.* 6(7)-*Chloro*-2 : 3-*diphenyl*-7(6)-*methylquinoxaline* (Formula IV).



(IV.)



(V.)

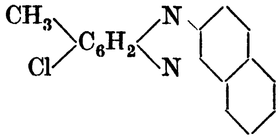
Three grams of benzil and 2 grams of 6-chloro-3 : 4-tolylenediamine dissolved in 30 c.c. of glacial acetic acid were heated at 100° for fifteen minutes, when white needles separated, the solution becoming nearly solid when cold. The product, when crystallised from alcohol and glacial acetic acid, separated in colourless needles melting at 148·5° and developing a red coloration with concentrated sulphuric acid (Found : N = 8·52. $C_{21}H_{15}N_2Cl$ requires N = 8·47 per cent.).

This quinoxaline derivative dissolved readily in hot petroleum (b. p. 80—100°), and was very soluble in benzene or chloroform.

6(7)-*Chloro*-7(6)-*methylquinoxaline*-2 : 3-*dicarboxylic Acid* (Formula V).

Potassium dihydroxytartrate (3·6 grams) was added slowly to a boiling solution of 6-chloro-3 : 4-tolylenediamine (2 grams) in 160 c c. of water and 40 c c. of alcohol. The faintly red solution was then acidified with concentrated hydrochloric acid, when a pale green, crystalline precipitate separated. This product was redissolved on boiling after the addition to the mother-liquor of 200 c c. of water. The pale greenish-yellow needles deposited from solution after filtering off a green by-product were recrystallised from water containing a small amount of alcohol and hydrochloric acid, when the substance melted at 173° with decomposition (Found : $N - 9{\cdot}41$; $H_2O = 12{\cdot}05$. $C_{11}H_7O_4N_2Cl,2H_2O$ requires $N = 9{\cdot}26$; $H_2O = 11{\cdot}90$ per cent.). The hydrated acid lost water at 110°, the anhydrous residue melting at 165°. Concentrated sulphuric acid developed an orange coloration.

10-*Chloro*-9-*methyl*-αβ-*naphthaphenazine*,



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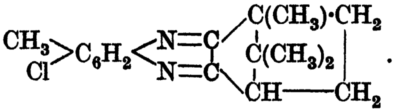
Two grams of the diamine dissolved in 200 c.c. of 50 per cent. acetic acid were added slowly with vigorous shaking to a solution of 2 grams of β-naphthaquinone in 140 c.c. of 75 per cent. acetic acid. The gelatinous precipitate which separated was crystallised from benzene, when the azine separated in brownish-yellow crystals with purple reflex, or from glacial acetic acid, when the product was obtained in brown needles melting at 213° (Found : $N = 10{\cdot}28$. $C_{17}H_{11}N_2Cl$ requires $N = 10{\cdot}06$ per cent.).

This azine developed an intense purple coloration with concentrated sulphuric acid.

6(7)-*Chloro*-7(6)-*methylcamphanoquinoxaline*,



Equal weights of camphorquinone and 6-chloro-3 : 4-tolylenediamine were boiled together in 15 per cent. alcoholic solution for a few minutes. The product precipitated by water was purified by repeated crystallisation from dilute alcohol. This quinoxaline formed colourless needles melting at 124° and developing with concentrated sulphuric acid a yellow coloration (Found: N = 9·92. $C_{17}H_{19}N_2Cl$ requires N = 9·77 per cent.; 0·4177 in 12·8 c.c. of alcoholic solution in a 1-dcm. tube gave $\alpha_D + 0{\cdot}91°$, whence $[\alpha]_D + 27{\cdot}9°$, corresponding with $[M]_D + 80°$.

Interaction of 6-*Chloro*-3 : 4-*tolylenediamine and Formaldehyde.*

1. *In Neutral Solution.*

Six c.c. of 40 per cent. formaldehyde solution, rendered neutral with two drops of *N*-sodium hydroxide, were added slowly to a solution of 3 grams of 6-chloro-3 : 4-tolylenediamine in 20 c.c. of boiling alcohol. After two or three minutes a precipitate appeared and spread throughout the liquid. This solid product, crystallised repeatedly from benzene, gave colourless, diamond-shaped crystals melting at 225°, the yield being 82 per cent. (Found: N = 15·65. $C_9H_9N_2Cl$ requires N = 15·52 per cent. Ebullioscopic determination in benzene gave M = 365·1, 369·6. $C_{18}H_{18}N_4Cl_2$ requires M = 361·2). These results confirm the dimeric formula I or Iᴀ for the substance.

*Tetramethylene*bis-2-*chloro*-4 : 5-*diaminotoluene* has the properties of a Schiff base and regenerates formaldehyde on warming with acids. The alcoholic mother-liquors from the foregoing Schiff base were diluted with water and the solution was extracted with ether. The residual oil from the ethereal extract deposited slowly a colourless solid which, after crystallisation from water, sublimed at 170° and melted completely at 175°. The compound, which is isomeric with the preceding substance, also undergoes hydrolysis with aqueous acids, liberating formaldehyde (Found: N = 15·54. Theory requires N = 15·52 per cent.).

2. *In Acid Solution.* 5-*Chloro*-1 : 6-*dimethylbenziminazole* (Formula III).

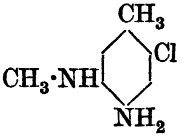
Concentrated hydrochloric acid (7 c.c.) and 40 per cent. formaldehyde solution (10 c.c.) were added successively to 5 grams of 6-chloro-3 : 4-tolylenediamine dissolved in 30 c.c. of alcohol; the hydrochloride of the diamine was precipitated and then redissolved and the resulting brown solution heated under reflux for thirty minutes. The cooled solution was rendered alkaline with dilute aqueous sodium hydroxide and the oil extracted with ether. The ethereal extract dried over potassium carbonate was distilled until a pale yellow oil passed over at 340—345°, which became solid and was then crystallised from benzene and light petroleum, when white needles were obtained melting at 154° (Found : N = 15·52. $C_9H_9N_2Cl$ requires N = 15·52 per cent. Ebullioscopic determination in benzene gave M = 203, 192. $C_9H_9N_2Cl$ requires M = 180·6). The *benziminazole* dissolved readily in alcohol or chloroform, but was almost insoluble in ether or light petroleum.

5-*Chloro*-6-*methylbenziminazole* (Formula II).

6-Chloro-3 : 4-tolylenediamine (5 grams) was heated for two hours at 100° with 5 c.c. of 80 per cent. formic acid; the base dissolved to a brown solution, which solidified on cooling. This product, which was the formate of the methenyl base, yielded this amidine on treatment with aqueous ammonia. The amidine, when crystallised from hot water, separated in colourless needles melting at 189° (Found : N = 16·85. $C_8H_7N_2Cl$ requires N = 16·82 per cent.).

The *amidine* dissolved readily in ether, alcohol, acetone, or hot water, but was almost insoluble in cold chloroform. The *formate*, prepared by adding formic acid to an ethereal solution of the base, separated from water in white, filamentous needles melting at 135° (Found: N = 13·23. $C_9H_9O_2N_2Cl$ requires N = 13·13 per cent.).

6-*Chloro*-3N-*methyl*-3 : 4-*tolylenediamine*,



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This compound was prepared by digesting 2-chloro-4 : 5-dinitrotoluene with alcoholic methylamine (this vol., p. 189) and by reducing the resulting 6-chloro-4-nitro-*N*-methyl-*m*-toluidine (4 grams) with 5 grams of 80 per cent. zinc dust in 100 c.c. of boiling alcohol (75 per cent.) containing 0·8 gram of ammonium chloride. This reduction was completed by refluxing for one hour with the further addition of 4 grams of zinc dust. The diamine separated slowly in pink needles on pouring the cold filtered solution into 500 c.c. of water containing 5 grams of sodium hydroxide (yield 75 per cent.). Owing to its great solubility in ordinary solvents the base was purified by sublimation in a vacuum, when colourless arborescent needles were obtained melting at 60° (Found : N = 16·55. $C_8H_{11}N_2Cl$ requires N = 16·43 per cent.).

When heated above its subliming point, this diamine became red and then changed into a dark bluish-purple decomposition product, sparingly soluble in water and dissolving readily in alcohol or mineral acids.

Action of Formic Acid on 6-Chloro-3N-methyl-3 : 4-tolylenediamine.—Equal parts of the diamine and concentrated formic acid were refluxed for two hours and the solution was rendered alkaline with ammonia. The solid product, which was somewhat discoloured, was crystallised repeatedly from benzene and identified as 5-chloro-1 : 6-dimethylbenziminazole (m. p. 154°).

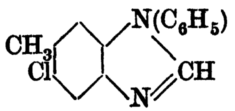
Action of Formaldehyde on 6-Chloro-3N-methyl-3 : 4-tolylenediamine.—*In Neutral Solution.*—The addition of 6 c.c. of 40 per cent. formaldehyde neutralised with two drops of *N*-sodium hydroxide to 3 grams of the diamine in 20 c.c. of alcohol led to a condensation product, which separated as a non-solidifying oil on dilution with water and was extracted with ether. As this oily material was not crystallisable from organic media, it was distilled, when at 340° a yellow oil was obtained which set to a yellow solid. This product, crystallised repeatedly from benzene, proved to be 5-chloro-1 : 6-dimethylbenziminazole, melting at 154° (formula III).

In Acid Solution.—To 3 grams of the diamine dissolved in 15 c.c. of alcohol were added successively 4·2 c.c. of concentrated hydrochloric acid and 6 c.c. of formaldehyde solution; the hydrochloride of the base separated and redissolved, the mixture becoming appreciably warm. After refluxing for thirty minutes, the mixture was rendered alkaline with potassium hydroxide, extracted with ether, and the extract dried over potassium carbonate. Dry hydrogen chloride was passed into the dried ethereal solution, when a tarry impurity separated and subsequently a crystalline dihydrochloride. This salt, washed with cold chloroform to remove coloured impurities, crystallised from the hot solvent in colourless needles melting with decomposition at 140° (Found: N = 10·49. $C_{10}H_{15}N_2Cl_3$ requires N = 10·40 per cent.).

The base could not be liberated by ammonia, but when freed with potassium hydroxide and crystallised from ether or petroleum (b. p. 80—100°), was obtained from the latter in colourless, rhomboidal plates melting at 100° (Found: N = 13·20, 13·16. $C_{10}H_{13}N_2Cl,H_2O$ requires N = 13·06 per cent.).

These results correspond with the following formulæ for base and dihydrochloride respectively: $CH_3\cdot C_6H_2Cl{:}[N(CH_3)]_2{:}CH_2,H_2O$ and $CH_3\cdot C_6H_2Cl{:}[N(CH_3)]_2{:}CH_2,2HCl$.

5-Chloro-1-phenyl-6-methylbenziminazole,



(VI.)

2-Chloro-4 : 5-dinitrotoluene was converted successively into 6-chloro-4-nitro-*N*-phenyl-*m*-toluidine and 6-chloro-3*N*-phenyl-3 : 4-tolylenediamine (this vol., p. 190). This diamine was refluxed for an hour with an equal weight of concentrated formic acid. The solution, which solidified on cooling, was rendered ammoniacal; the solid product was crystallised first from alcohol with addition of animal charcoal and then repeatedly from petroleum (b. p. 80—90°). The amidine separated in colourless needles melting at 100° (Found: N = 11·81. $C_{14}H_{11}N_2Cl$ requires N = 11·55 per cent.).

[With F. R. JONES.]

6-*Chloro*-4-*nitro*-m-*toluidine*, m. p. 158—159°.

Preparation of 6-*Chloro*-m-*toluidine*.

1. From 2-Chloro-5 : 6-dinitrotoluene.—This dinitro-compound was converted successively into 6-chloro-3-nitro-*o*-toluidine and 2-chloro-5-nitrotoluene (Morgan and Drew, T., 1920, **117**, 787). This nitro-compound on reduction yielded 6-chloro-*m*-toluidine (m. p. 85°).

2. From *p*-Toluenesulphon-*o*-toluidide.—*o*-Toluidine was converted into its *p*-toluenesulphonyl derivative (m. p. 108°); 20 grams of the latter suspended in 50 c.c. of water at 60° were treated with 20 c.c. of nitric acid (D 1·4), the mixture being stirred at 60—70° for three to four hours. The product recrystallised from alcohol was *p*-toluenesulphon-5-nitro-*o*-toluidide (m. p. 172°). If the foregoing temperatures are exceeded, further nitration occurs, so that after hydrolysis the product contains 3 : 5-dinitro-*o*-toluidine (m. p. 208°) and a small amount of 3-nitro-*o*-toluidine. The mononitrated amide (10 grams) was dissolved in 60 c.c of concentrated sulphuric acid on the water-bath. The cooled solution, when poured into 200 c.c of water and rendered alkaline, yielded 5-nitro-*o*-toluidine, which was recrystallised from hot water (m. p. 130°). This base, when put through the Sandmeyer reaction with cuprous chloride, gave 2-chloro-5-nitrotoluene, which on reduction yielded 6-chloro-*m*-toluidine.

Nitration of 6-Chloro-aceto-m-*toluidide*.

6-Chloro-*m*-toluidine (2 parts) was heated for one hour with 1 part of acetic anhydride mixed with an equal weight of glacial acetic acid. The acetyl derivative, when crystallised from petroleum, melted at 92°. Five grams of this acetyl compound were added slowly to a mixture of 4 c.c. of nitric acid (D 1·40) and the same volume of fuming nitric acid (D 1·50). After sixteen hours, the solution, when poured into water, gave an oil solidifying very quickly to a golden-yellow solid, which, after crystallisation from alcohol, melted at 113°. One gram of this acetyl compound was dissolved in 6—8 c.c. of concentrated sulphuric acid by raising the temperature cautiously to 130°. After being maintained for a few minutes at this temperature, the solution was cooled and poured into 250 c.c. of water, when an orange-yellow nitro-base was obtained, the precipitation being completed by the addition of ammonia. After crystallisation from alcohol 6-chloro-4-nitro-*m*-toluidine separated in yellow prisms melting at 158—159°.

*Mixed Melting Points of 6-Chloro-4-nitro-*m*-toluidine and 6-Chloro-3-nitro-*p*-toluidine.*

6-Chloro-3-nitro-*p*-toluidine (m. p. 165°) was prepared by the following processes: nitration of *o*-toluidine; conversion of 4-nitro-*o*-toluidine into 2-chloro-4-nitrotoluene, reduction to 6-chloro-*p*-toluidine, nitration of 6-chloro-aceto-*p*-toluidide, and hydrolysis of the nitro-product.

Mixed melting points were taken with mixtures of the two isomeric bases with the following results:

Percentage of the more fusible base (158·5°) in the mixture . . .	100	90	80	70	60	50	40	30	20	10	0
Melting point of the mixture . . .	158·5°	152·5°	148°	14[illegible]·5°	140·5°	139·5°	139°	141°	147·5°	156°	164·5°

It is evident that the preparation melting at 144° recorded in Part I of this communication (*loc. cit.*) is a mixture consisting approximately of 73 per cent. of 6-chloro-4-nitro-*m*-toluidine and 27 per cent. of 6-chloro-3-nitro-*p*-toluidine. This conclusion was confirmed by taking mixed melting points of a mixture of the pure bases in the foregoing proportions with the preparation melting at 144°; the observed melting points were 143·5—146° and 144—146°. This constancy of melting point indicated identity of composition in the two mixtures, whether obtained by mixing the pure isomerides or by acting on 2-chloro-4:5-dinitrotoluene with alcoholic ammonia.

6-Chloro-4-nitro-*m*-toluidine from 6-chloro-*m*-toluidine was methylated and phenylated under the experimental conditions described in Part II of the communication (this vol., p. 189—190). The melting points of the products, 6-chloro-4-nitro-*N*-methyl-*m*-toluidine and 6-chloro-4-nitro-*N*-phenyl-*m*-toluidine, were 126° and 96° respectively, showing that these compounds are identical with the chief products of the action of methylamine and aniline on 2-chloro-4:5-dinitrotoluene.

The authors desire to express their thanks to the Advisory

Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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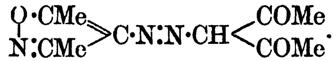
CLXXXI.—*Non-aromatic Diazonium Salts. Part VII. The Diazo-reaction in the* iso*Oxazole Series.*

By GILBERT T. MORGAN and HENRY BURGESS.

4-AMINO-3 : 5-DIMETHYL*iso*OXAZOLE has been shown recently (this vol., p. 697) to give rise to diazonium salts comparable in stability with those derived from aniline and its homologues. The reactions of 3 : 5-dimethyl*iso*oxazole-4-diazonium chloride have now been examined further with the object of ascertaining to what extent the *iso*oxazolediazonium salts can be used as synthetic agents.

Non-aromatic azo-derivatives are obtainable by coupling the diazonium salt with the β-diketones and β-ketonic esters.

3 : 5-*Dimethyl*iso*oxazole-4-azo-acetylacetone*,



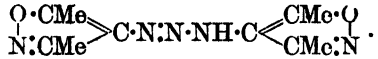
$$\begin{matrix}\mathrm{O{\cdot}CMe}\\ |\\ \mathrm{N{:}CMe}\end{matrix}>\mathrm{C{\cdot}N{:}N{\cdot}CH}<\begin{matrix}\mathrm{COMe}\\ \mathrm{COMe}\end{matrix}.$$

One gram of 4-amino-3 : 5-dimethyl*iso*oxazole in 5 c.c. of concentrated hydrochloric acid was cooled in a freezing mixture and diazotised by adding slowly 0·7 gram of sodium nitrite; the diazo-solution was then added to one gram of acetylacetone in 8 c.c. of 12 per cent. aqueous sodium hydroxide. The precipitation of the lemon-yellow azo-derivative was completed by salting out (yield 80 per cent.). After several crystallisations from alcohol, the compound was obtained in well-defined, yellowish-orange, hexagonal prisms melting at 115·5—116·5° (Found: N = 19·05. $C_{10}H_{13}O_3N_3$ requires N = 18·83 per cent.).

3 : 5-*Dimethyl*iso*oxazole-4-azo-acetylacetone* was very soluble in cold aqueous caustic alkalis, hydrochloric acid, glacial acetic acid, and the ordinary organic media excepting light petroleum; it dissolved sparingly in hot water, but was insoluble in cold water. On warming, it reduced Fehling's solution and gave neither colour

reaction with ferric chloride nor copper salt with neutral copper acetate.

4-*Diazoamino*-3 : 5-*dimethyl*isoo*xazole*,



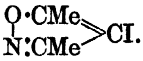
$$\begin{array}{l}O\cdot CMe\\ N{:}CMe\end{array}\!>C\cdot N{:}N\cdot NH\cdot C<\!\begin{array}{l}CMe\cdot O\\ CMe{:}N\end{array}\cdot$$

A diazo-solution prepared as above from one molecular proportion of the amino*iso*oxazole hydrochloride was added to an aqueous solution of the base (1 mol.) and sodium acetate (5 mols.). The pale brown product, precipitated completely by adding sodium chloride, was crystallised from a mixture of equal parts of acetone and light petroleum, from which solution the diazoamine first separated in colourless, transparent, hexagonal prisms which did not change if removed from the solvent. If left in contact with the mother-liquor, however, for several days, these prismatic crystals changed into small, opaque, white octahedra. Both forms of the diazoamine melted at 179—180° (Found: N = 29·93; C = 51·05; H = 5·70. $C_{10}H_{13}O_2N_5$ requires N = 29·77; C = 51·02; H = 5·57 per cent.).

4-*Diazoamino*-3 : 5-*dimethyl*isoo*xazole* was soluble in the ordinary organic media excepting light petroleum; it dissolved in hot water or in aqueous caustic alkalis, and was reprecipitated from the latter by acids. It was very stable towards hydrolytic agents, and was not decomposed by cold concentrated hydrochloric acid.

iso*Diazo-reaction.*—A cold solution of 3 : 5-dimethyl*iso*oxazole-4-diazonium chloride (0·7 gram) was added slowly to 7 grams of sodium hydroxide in 6 c.c. of water. A reddish-pink precipitate appeared, but redissolved to a deep red solution, the temperature rising to 20°. This solution coupled with alkaline β-naphthol only in the course of several hours, but if first cautiously acidified it coupled immediately. The alkaline solution slowly lost its coupling power and on passing carbon dioxide into this solution a brown oil separated, which no longer coupled even after acidifying.

4-*Iodo*-3 : 5-*dimethyl*isoo*xazole*,



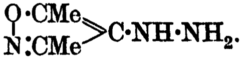
$$\begin{array}{l}O\cdot CMe\\ N{:}CMe\end{array}\!>CI.$$

As the chloro- and bromo-*iso*oxazoles appeared to be oily substances like the 4-triazo-compound (*loc. cit.*, p. 782), the iododerivative was prepared in order to demonstrate the replacement of the diazo-group by a halogen. The diazonium sulphate from 1 gram of aminodimethyl*iso*oxazole was added to 7 grams of potassium iodide in 10 c.c. of water. Rapid effervescence occurred and a reddish-brown oil separated having an odour like that of iodoform, but more lachrymatory. After two hours, the mixture was distilled in steam and the distillate freed from iodine by sodium hydroxide.

4-*Iodo*-3 : 5-*dimethyl*iso*oxazole*, when purified by repeated distillation in steam, separated in very pale yellow needles melting at 52·5—54° (Found : I = 57·47. C_5H_6ONI requires I = 56·93 per cent.).

This iodo-derivative was very soluble in ether, acetone, chloroform, or benzene, but less soluble in alcohol or hot water. It was extremely volatile, distilling in the vapour of acetone, and when left for four days over sulphuric acid about one-third of the preparation had volatilised. It was accompanied by a small amount of less volatile by-product separating in golden-yellow needles melting at 181—182° and containing no iodine. When pure, 4-iodo-3 : 5-dimethyl*iso*oxazole is only faintly odorous, although distinctly irritant to the eyes.

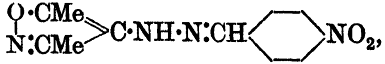
4-*Hydrazino*-3 : 5-*dimethyl*iso*oxazole*,



$$\begin{array}{l}\mathrm{O{\cdot}CMe}\\ \mathrm{N{:}CMe}\end{array}\!\!>\!\mathrm{C{\cdot}NH{\cdot}NH_2}.$$

To a cold solution of 3 : 5-dimethyl*iso*oxazole-4-diazonium chloride prepared from 2 grams of the base were added 11 grams of stannous chloride dissolved in 8 c.c. of concentrated hydrochloric acid. A yellow, frothy precipitate, which first appeared, redissolved on stirring to a yellow solution, which was cooled to — 5°. The solution was made alkaline with sodium hydroxide and the hydrazine extracted with chloroform. This extract, when dried over sodium sulphate and evaporated at the ordinary temperature, left a pale green solid melting at 65—72° and having a strong odour resembling that of dimethyl*iso*oxazole. In subsequent experiments the viscous residue from the chloroform was dissolved in alcohol and warmed on the water-bath with *p*-nitrobenzaldehyde (1 mol.). The resulting hydrazone separated as a brick-red precipitate and was crystallised from alcohol in garnet-red, highly refractive prisms having a tough resinous fracture and melting at 183—184° (Found : N = 21·33. $C_{12}H_{12}O_3N_4$ requires N = 21·53 per cent.).

4-p-*Nitrobenzylidenehydrazino*-3 : 5-*dimethyl*iso*oxazole*,



$$\begin{array}{l}\mathrm{O{\cdot}CMe}\\ \mathrm{N{:}CMe}\end{array}\!\!>\!\mathrm{C{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2},$$

was soluble in ether, alcohol, chloroform, benzene, or acetone. A dilute solution of the hydrazone in the last of these solvents assumed an intense greenish-blue colour on the addition of concentrated aqueous sodium hydroxide; this coloration, which is probably due to the formation of a highly coloured sodium salt of the type $[C_5H_6ON]\cdot NH\cdot N{:}C{:}C_6H_4{:}NO\cdot ONa$, is destroyed by acids and even by carbon dioxide or water.

Attempts to replace the diazonium group by ethoxyl or hydroxyl did not lead to the expected result. In the latter case about 20 per cent. of a solid product was obtained crystallising in colourless, transparent plates or lath-like needles melting at 139—140° (Found: N = 25·49, 25·56 per cent.). This substance, which contains approximately the same amount of nitrogen as the original aminodimethyl*iso*oxazole, was also obtained in an attempt to replace the diazo-complex by a sulphinic group.

Summary.

1. The foregoing experiments, in addition to those of the earlier communication (*loc. cit.*), show that the diazonium group, when attached to an *iso*oxazole ring, is replaceable by the halogens and by the triazo-group, but not by hydroxyl, ethoxyl, or sulphinic groups.

2. In alkaline solutions an unstable *iso*diazo-compound is produced.

3. Reduction of the diazonium chloride leads to an unstable 4-hydrazinodimethyl*iso*oxazole.

4. *iso*Oxazolediazonium salts couple with bases to form diazoamino-derivatives and with phenols and β-diketones to yield mixed aliphatic–aromatic and non-aromatic azo-derivatives respectively.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

THE CHEMICAL DEPARTMENT,
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EDGBASTON.

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CLXXXII.—*A New Type of Iodine Compound.*

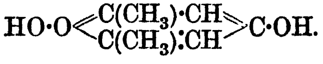
By JOHN NORMAN COLLIE and AMY ADA BEATRICE REILLY.

WHEN dimethylpyrone is boiled with excess of barium hydroxide, the yellow barium salt of diacetylacetone is precipitated. If this salt is suspended in alcohol and treated with iodine, it first dissolves, and on warming a crystalline barium salt separates which does not further react with iodine. The reaction ceases when two atoms of iodine have been added for each atom of barium. Only one-half of the iodine reacts to form barium iodide, the other half reacts with the diacetylacetone, for the barium salt that separates, when treated with dilute acids, gives a compound $C_7H_7O_3I$ (T., 1900, **77**, 1116).

It is difficult to give an explanation how the compound $C_7H_7O_3I$ is formed from the barium salt of diacetylacetone by the action of iodine.

If all the dimethylpyrone, $C_7H_8O_2$, is acted on by the iodine, and converted into $C_7H_7O_3I$, the yield should be four times the amount always obtained. Moreover, only half the barium in the barium salt is acted on by the iodine. Therefore the barium salt of diacetylacetone must contain at least two barium atoms in the molecule, and they must be linked differently. The ordinary formula for diacetylacetone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, will not allow of any such difference.

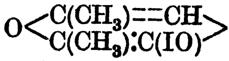
The above formula for diacetylacetone also does not agree with some of its physical properties. This was pointed out (T., 1905, **87**, 1451). Moreover, other properties and reactions are not satisfactorily explained by the above formula. Amongst organic compounds there is always a tendency to form ring compounds whenever possible, and it may be that diacetylacetone is a ring compound,



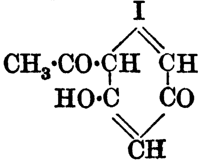
$$HO{\cdot}O{<}\begin{matrix}C(CH_3){\cdot}CH\\C(CH_3){:}CH\end{matrix}{>}C{\cdot}OH.$$

Such a formula would give a barium salt, where the barium atoms would be linked in two different ways, one to the oxygen of the hydroxyl group attached to oxygen, and one to the hydroxyl group attached to carbon. Iodine might only react with the barium replacing the hydrogen of the hydroxyl group attached to the oxygen.

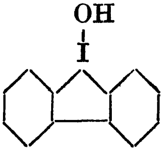
The reaction of iodine with the barium salt of diacetylacetone, moreover, is different from the action of iodine with the sodium salt of acetylacetone, that gives tetra-acetylethane. In the reaction producing the compound $C_7H_7O_3I$ there must be an oxidising action. It may be that the barium in the barium salt of diacetylacetone reacts in the same way as barium hydroxide does with iodine, giving a mixture of iodide and hypoiodite, the latter acting as the oxidising agent. But there does not seem to be any simple equation that will explain the formation of the compound $C_7H_7O_3I$. Moreover, from its properties and reactions it is no simple derivative either of diacetylacetone or of dimethylpyrone.

It might be iodosodimethylpyrone,  $O<\begin{matrix}C(CH_3)=CH\\C(CH_3):C(IO)\end{matrix}>CO$, but it is not decomposed by sodium hydroxide, and all pyrone compounds are. It might be iodoso-orcinol, but it gives no orcinol reactions. It is neither a hypoiodite nor an iodo-compound. It is a strong acid liberating carbon dioxide from carbonates and forms metallic salts, but the iodine is easily removed as silver iodide when warmed with silver nitrate and nitric acid; it can, however, be boiled with concentrated sodium hydroxide solution without decomposition. Chlorine water does not liberate iodine. From its acid properties it contains either a carboxyl group or an I·OH group. The presence of a carboxyl group is not possible. It gives a monoacetyl derivative, and reacts with two molecules of phenylhydrazine.

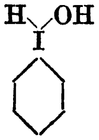
The only simple formula that agrees with most of its properties and reactions is the following:



When it dissolves in water the iodine atom becomes quinquevalent, taking up the elements of water. Ring compounds containing iodine are not novel. Mascarelli (*Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 580; *Gazzetta*, 1908, **38**, ii, 619) describes one that is a strong base capable of absorbing carbon dioxide from the air.



Basic.



Acid.

That iodine in a ring with four carbon atoms should be basic, and in a ring with five carbon atoms should be acid, is behaviour exactly the reverse of that of nitrogen in pyrrole and pyridine. The remaining reactions of the compound $C_7H_7O_3I$ are the following:

With an excess of bleaching powder solution it gives a precipitate of calcium carbonate. The amount was estimated, (1) as carbon dioxide (Found: C = 14·2), (2) the carbon dioxide absorbed by potassium hydroxide (Found: C = 13·5), (3) as precipitated calcium carbonate (Found: C=13·5). Theory for three atoms of carbon C=13·5 per cent.

When boiled under reflux with very dilute sulphuric acid, it gradually decomposes, giving acetic acid, hydriodic acid, and some substance that chars with concentrated sulphuric acid, and reduces Fehling solution, and also gives a precipitate with phenylhydrazine. The substance, however, does not seem to be a sugar, for it can be extracted slowly by means of ether, but it has not been obtained in a crystalline condition.

When heated with water at 130—140°, the substance $C_7H_7O_3I$ decomposes almost quantitatively into hydriodic acid, acetic acid, carbon, and water, as follows, $C_7H_7O_3I + H_2O = HI + CH_3{\cdot}CO_2H + 5C + 2H_2O$; 0·936 gave 0·198 C, 0·432 HI, 0·202 $CH_3{\cdot}CO_2H$, the theoretical amounts being 0·211 C, 0·450 HI, 0·211 $CH_3{\cdot}CO_2H$. It is not, however, decomposed by boiling water. It is a monobasic acid, for when titrated with $N/10$-sodium hydroxide it forms a salt;

$$C_7H_7O_3I + NaOH = C_7H_8O_4INa.$$

The mean of three molecular-weight determinations by the freezing point method gave M = 263. $C_7H_7O_3I$ requires M = 266.

When the substance is boiled with dilute alcohol and sodium amalgam, the iodine is quantitatively removed as sodium iodide, and this is the simplest method of estimating the iodine in the substance and its compounds.

With potassium iodide and a dilute acid, it gives no free iodine. It can be dissolved in warm concentrated sulphuric acid without decomposition, and is reprecipitated on the addition of water, but if a strong mineral acid and a little water be used, iodine is at once liberated.

With bromine in chloroform solution, the bromine is at once decolorised and hydrobromic acid evolved, and the residue on boiling with dilute alcohol gives bromoacetone. With ferric chloride, it gives a deep purple precipitate. It decolorises potassium permanganate at once in the cold.

With a mixture of silver nitrate and nitric acid, about 95 per cent. of the iodine is converted into silver iodide.

When dry and pure, light has very little action on it, but when moisture is present, it rapidly decomposes, giving acetic acid and other compounds.

EXPERIMENTAL.

The best method for the preparation of the compound $C_7H_7O_3I$ is the following:

Ten grams of dimethylpyrone are boiled with excess of barium hydroxide, the precipitated barium salt is dried and suspended in 150 c.c. of absolute alcohol, and 20 grams of iodine are carefully added with shaking. The barium salt gradually dissolves and then another barium salt begins to crystallise out. It is not necessary to separate this barium salt. About 500 c.c. of water are then added and some dilute hydrochloric acid. The compound $C_7H_7O_3I$ at once separates. By making the mother-liquor alkaline with sodium hydroxide, evaporating off the alcohol, and acidifying again, a further small amount of the compound $C_7H_7O_3I$ is precipitated. It is necessary to make the solution alkaline before evaporation because the compound $C_7H_7O_3I$ is volatile with steam.

From the residue a small amount of dimethylpyrone, and a compound that gives a deep purple colour with ferric chloride, can be extracted.

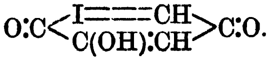
The pure compound $C_7H_7O_3I$ can be obtained by crystallisation from dilute alcohol or from acetic acid. It seems to crystallise in two different forms, first separating as voluminous, needle-shaped crystals, that gradually change to small, granular crystals.

A number of analyses gave the following results: Mean, C = 31·5; H = 2·5; I = 47·1. $C_7H_7O_3I$ requires C = 31·6; H = 2·6; I = 47·7 per cent. The yield of the compound is usually about half the weight of the dimethylpyrone employed. If all the dimethylpyrone were converted into $C_7H_7O_3I$, 10 grams should yield 21·4 grams; as a rule, only 5 grams are obtained.

When moist $C_7H_7O_3I$ is exposed to sunlight, it decomposes rapidly, turning brown and liquefying, and acetic acid is formed in considerable quantities. The brown mass, when treated with absolute alcohol, leaves an orange-red precipitate. This substance can be dissolved in hot acetic acid and is precipitated in small crystals by the addition of water. When heated, it turns brown and decomposes violently at 185—190° with liberation of much iodine. It is acid to litmus, is easily soluble in sodium hydroxide solution, and does not contain water of crystallisation. Unfortunately, only small quantities of it could be obtained, and only an iodine estimation was made (Found: I = 54·0. $C_5H_3O_3I$ requires I = 53·4 per cent.). It may have been formed according to the equation

$$C_7H_7O_3I + H_2O + O_2 = C_5H_3O_3I + CH_3{\cdot}CO_2H + H_2O,$$

when it would have the quinonoid formula



$$\mathrm{O{:}C}<\begin{array}{c}\mathrm{I{=\!=\!=}CH}\\ \mathrm{C(OH){:}CH}\end{array}>\mathrm{C{:}O}.$$

The *barium compound* that separates when iodine is added to the barium salt of diacetylacetone, crystallises in needles. It is insoluble in water, and when treated with dilute acids gives the compound $C_7H_7O_3I$. On heating, it decomposes, giving iodine. It contains water of crystallisation [Found, for material dried in a desiccator, $Ba = 19{\cdot}5$; $I = 36{\cdot}4$; $H_2O = 5{\cdot}5$. $(C_7H_6O_3I)_2Ba,2H_2O$ requires $Ba = 19{\cdot}5$; $I = 36{\cdot}1$; $H_2O = 5{\cdot}1$ per cent. Found, for material dried at 140°, $Ba = 20{\cdot}7$. $(C_7H_6O_3I)_2Ba$ requires $Ba = 20{\cdot}5$ per cent.].

Acetyl Derivative.—By heating the compound $C_7H_7O_3I$ with acetic anhydride and a few drops of concentrated sulphuric acid, and then adding water, a semi-crystalline precipitate is obtained. This can be purified by dissolving in alcohol, decolorising with animal charcoal, and recrystallising. It forms white, granular crystals, m. p. 68·5°. It gives no colour with ferric chloride, and is acid to litmus paper. It can be distilled without decomposition. On keeping, it turns bright lemon-yellow, finally becoming orange. The mean of several analyses gave $C = 34{\cdot}6$; $H = 3{\cdot}0$; $I = 41{\cdot}1$. $C_7H_6O_3I(CO{\cdot}CH_3)$ requires $C = 35{\cdot}1$; $H = 2{\cdot}9$; $I = 41{\cdot}2$ per cent. When the acetyl derivative is warmed with sodium hydroxide solution and the product acidified, the compound $C_7H_7O_3I$ is precipitated.

Phenylhydrazine Derivative.—The compound $C_7H_7O_3I$ reacts violently with phenylhydrazine, and water is given off. If, however, it is dissolved in a little alcohol and phenylhydrazine added, the mixture becomes warm, and a crystalline compound separates. It can be recrystallised from acetic acid. On heating, it rapidly turns brown and suddenly decomposes. It contains water of crystallisation, but decomposes below 100° [Found: $N = 11{\cdot}3$; $I = 25{\cdot}0$. $C_7H_7OI(N_2H{\cdot}C_6H_5)_2,3H_2O$ requires $N = 11{\cdot}2$; $I = 25{\cdot}4$ per cent.].

Salts of the Compound $C_7H_7O_3I$.—The compound was treated with excess of barium hydroxide, the excess being removed with carbon dioxide. The filtered solution was evaporated to a small bulk and alcohol added. The salt separated in long, white needles. These, when dried in a vacuum over sulphuric acid, turned lemon-yellow. The mean of several analyses gave $Ba = 19{\cdot}7$; $I = 35{\cdot}8$. $(C_7H_8O_4I)_2Ba$ requires $Ba = 19{\cdot}5$; $I = 36{\cdot}1$ per cent.

The *silver* salt is insoluble in cold water and slightly soluble in hot water. The *lead* salt has similar solubilities.

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Photosynthetic Processes in the Air, upon the Land, and in the Sea in Relation to the Origin and Continuance of Life on the Earth.

HUGO MÜLLER LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON JUNE 16TH, 1921.

By BENJAMIN MOORE, D.Sc., F.R.S.

MR. PRESIDENT, LADIES and GENTLEMEN,—In the course of this lecture I am about to attempt to summarise ten years' work. I should like at the outset to express my gratitude to several collaborators who have aided me on the subject—especially to my friend Mr. Edward Whitley, of Oxford, and to Mr. Arthur Webster, of London, who have assisted me throughout these researches.

The results obtained may be of practical interest to the botanist and to the chemist, and even to the economist; but it is not from any of those practical aspects that I would like to present the subject to you this evening, but rather from a philosophical point of view. The outset of the whole matter is:—How did living things come to be on this earth or on any other earth? It is a curious thing that I am standing up here talking to you this evening and that you are all listening to me, if you will reflect upon it that some millions of years ago this earth was a molten mass. Many theories have been put forward to explain how life did come to the earth, and how it could come to the earth. Some only pass on the problem to another world, and say that a germ was born in that distant world—that, either by radioactivity or by sunlight, or in some other way, this germ landed upon our earth, and so, by a fortuitous combination of circumstances, we are all here. There is not any modern theory which passes that limit. All the earlier theories as to how life arose seem to be lacking in that they do not start at the beginning of things. That is not to be wondered at. In the days of van Helmont, the Abbé Spallanzani, and those who succeeded them, and even in the days of Pasteur, people were seeking for a sudden evolution of life. That is not a philosophical point of view. Life is not distinct from the inorganic. Any germ arriving from another planet must have had the property of building up energy, or it could not have existed. Therefore there must be supplied some stages that lie between anything, even so simple as the single unicellular alga, and the inorganic world. There must be some possibility of tracing out a continuity right through from the inorganic to the organic and up to man.

It is a remarkable fact that evolution was first discovered in the organic world. It might at the outset seem probable that the chemist would be the first to discover evolution, but he was not. It was the biologist who discovered evolution, and the chemist is following in his footsteps.

It appears to me that the fundamental law in all evolution is the law of what might be called "complexity,"—that as soon as it becomes possible for matter to become more complex under the energy field in which it exists it obeys the law and becomes more complex.

In the sun, for example, even binary compounds probably do not exist at all. From all that astronomy and spectroscopy teach us, even such a stable element as iron is broken up into proto-elements. But as the inorganic environment changes it becomes possible for elements, as we know them on earth, to exist, and, at a later stage, it becomes possible for simple binary compounds also to exist. Always Nature proceeds on this law of complexity to a point at which, as will now be shown, it becomes necessary to establish a new unit.

I am not going to attempt to enter into the construction of the atom. I do not know enough to do so. But it seems that the electron is about the simplest thing possible. The electron, with some central basis and with a number of other electrons variously arranged, forms the atoms. The atom goes on evolving in complexity, and as it gets heavier and heavier and more complex there comes a period at which that unit reaches its maximum and as it reaches its maximum the element becomes unstable. It is just here that there appear the radioactive elements. But Nature is not to be baffled by this new situation. She proceeds to the simple inorganic compound, and she makes mono-molecules of the simplest type. Then she goes on and on with these until a new limit is reached. She adds on to the mono-molecules subsidiary molecules, such as the water of crystallisation, and, finally, a stage is reached at which fresh building up is impossible. It is not always reached at the same place, but a point in the average is reached where she cannot build up more complex molecules, and she then begins to build up colloids. She takes even quite simple molecules like silica (SiO_2) and combines these into groups of fifty or sixty molecules. These acquire different properties as they go on. They become what Graham called metastable. Their reactions are much slower than those of the simple inorganic compounds, and so we pass on towards life. Always Nature is phasic, and the periodicity of movement becomes slower as the organism becomes larger and larger; and it is as it reaches these larger stages that it begins to react with outside forms of energy in a new manner.

It is curious that at the lower temperatures of the air radiant energy can come from the sun and build itself up again and form things like coal and petrol and all those combustible things from which one can make high explosives.

As the colloid becomes more complex it acquires the power to react to the light, and it is only when a stage has been reached at which reaction to light can occur that it becomes feasible to build up living creatures. If you reflect about it, it is really strange how biochemical energy, the energy of life, comes into everything. I do not believe there is a single object in this room that has not had biochemical energy concerned in the formation of it. Let us take this glass. How could that bottle have been made if there were not the energy of biochemistry to fasten the silicates into it? Ourselves, our clothes, the table in front of me, paper, everything practically that man is concerned with, arose from light. Light was the beginning of all things living: there is no question about that. And it was in the water that they began. Three-fourths of our own bodies consist of water now. Nothing happens within our bodies that does not happen in solution. It was in the sea and in the lakes that life first originated by the bearing down of the sun's energy upon these inorganic colloidal complexities which were beginning to form there.

Then there was adsorption as in the diatom. These inorganic colloids not only form the organic matter, but they build it up into their own cells; they form skeletons for it. And so we can trace, if we commence at these beginnings, how life began. We shall never trace it by studying bacteria. Bacteria could not exist in this new world. There is nothing for them to live on. There is no food for them. The condition is a thousand times worse than a coal strike; there is nothing to eat even. Nothing living could arise under such conditions that did not possess the property of building up the energy of the sunlight as it came down to it. It is an interesting discovery that in those early days it was the ultra-violet and the blue light that were used, just as a photographic plate uses these rays to-day, and as evolution has proceeded there have appeared more and more delicate sorts of transformers which must even be carefully protected from such rays and utilise instead the slower waves of the spectrum. As you all know, sunlight is germicidal to bacteria; they cannot be exposed to it, and so various colour screens have to be fabricated, such as chlorophyll, and many others, which protect this dawning life from being killed by the very sunlight which first originated it. Also it does not seem to have been the purpose of Nature, or whatever governs Nature, merely to evolve life, because several other changes, which will now be considered, had to occur before life became possible down below.

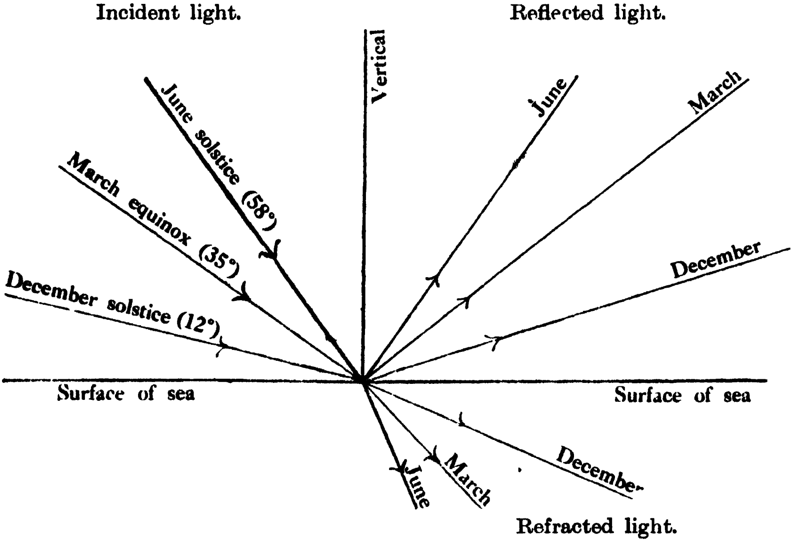
Let us think of the thing at the beginning. As the light from the sun first strikes the earth's atmosphere, perhaps one or two hundred miles above, it is full of ultra-violet light, and violet light. Such light rays as these, if they reached the earth at the present moment, would annihilate us; they would simply mean death to the world below.

The first thing that happens to prevent this is that ozone is developed, and by absorption this ultra-violet light is shut out. The solar spectrum of sunlight was known to the physicists to be marked out, to be limited, by the ozone developed in the upper atmosphere, and it has been shown that if there were only a millimetre of ozone interposed between quartz plates nearly all this light, which is germicidal light, would be shut out. It is not completely shut out as the light passes through the air and that is why there must be these natural colour screens in plants and animals and man. Bacteria cannot live in the open in the sunlight, and, as Marshall Ward showed, those fungi that live in the open and are not under the protection of green trees have to possess some colour developed within them, some pigment, so that this light is shut out.

Another interesting field and one that wants investigation, is the effect of short wave-lengths of light on various gaseous mixtures. For example, nitrogen and oxygen unite under the influence of light, it is true only to a small extent, but they do combine and form nitrogen pentoxide and nitrogen trioxide. Also from nitrogen and hydrogen ammonia can be produced. All these changes are of great importance in the atmosphere, before the earth or the sea is approached.

Next, let us consider the sea, where life first started, and where, in the vegetable world, it has only in a comparatively small number of species got beyond the algal region yet. The reason why algæ still form the preponderating bulk of marine plant life probably is that the external medium (sea water) gives perfect nourishment to the alga; it was when plants passed to new environment that further evolution was required to conserve the store of alkali. This conservation of alkali evolved in fresh water as a preliminary to terrestrial life. It is light then that produces the change in the springtime, and not temperature. At the end of this lecture I will show you a slide to demonstrate that clearly. When the temperature is at its lowest in the sea a tide of life suddenly bursts forth. As the spring advances the sun is getting higher every day, and the day is getting longer, and one can easily perceive that what might be called a critical angle is reached. I will draw what I mean on the blackboard. Take this line to represent the surface of the sea, this arrow the light, and on a November or December day the sunlight is coming upon the sea surface. Not only is the day short and the light feeble, but practically none of the light will pass through. Now come to the equinox about March. Then the light breaks through into the sea, and just at that period there is a wonderful outburst of life before the temperature has risen at all. That is a most remarkable and interesting thing, and also a fact of practical importance, because, until that light comes to the sea, producing the minute floating green plants, the life of the crustacean leading up to the life of the herring and the food fishes cannot appear. This action of light is the beginning of the whole Spring in the sea. At a certain time the light penetrates into the sea water, and a day or two later the great sea breaks out into life, and there is a long concatenation of generations after that which lead up to the varied life of the sea. The amount of alkali developed as that light enters the sea and acts upon the floating algæ suffices to turn the sea water alkaline to the most delicate indicator. Calcium bicarbonate and magnesium bicarbonate are taken out of the water,

FIG. 1.



This sketch illustrates the direction and intensity of light entering the sea at various seasons of the year at a latitude of 55° North. The sun's declination in June solstice being 23½° the altitude at noon is (90−55)+23½=58½°, at the equinox in March the altitude is 90−55=35°, and in the December solstice it is 35−23½=12½° only. The variation in the length of the day is also to be remembered. The optimum daily exposure is that of the spring; winter is too dark and summer too bright.

and the normal carbonates are turned into the sea, and so there is produced a strongly alkaline solution, especially at isolated places, like pools on the shore at low tide. I think this has a good deal to do with the annual beginnings of life. A different reaction arises in the sea water, and it is just about then that reproduction commences. It is really an intensely interesting change, and one that does not happen on land or in higher fresh-water plants. By examining the reaction of the sea water it can be determined what the crop of the sea is going to be. There can be calculated the number of cubic metres of sea water on which the sunlight acts. The action of photosynthesis probably descends for about 30 or 40 metres, and if quantities be calculated out it is found that round our shores there is as big a crop of green matter as there is on the land, and this sea-crop is all eaten up by one generation of creatures after another, and all the life of our seas, and all our fish, depend on that simple circumstance, that at a certain time in the year there is a sufficient amount of light going into the water to fire off this whole train of events. The variation is quite seasonal; you get it best in Spring, and then as you go on to July or August it falls off. There is too much light. Things get killed off in July and August, but at the spring equinox, and again, but in lessened degree, at the autumnal equinox, there is reached the largest amount of this photosynthesis occurring in the sea.

If we pass on to the land, a very interesting question confronts us. For years I have gone round in the woods looking at the dry twigs in the winter time, and wondering to myself how different they are when they burst out into green in the Spring. What is it that happens? The orthodox botanist will tell you that it was due to last year's storage, that last year the trees stored up some material and this suddenly bursts out in the Spring as the temperature rises. If you cut twigs and examine into the matter with a critical eye, you will find there is very little storage in the ordinary plant or tree. It puzzled me for a long time, and I do not know that I understand it yet, but I will tell you what my thoughts are. Every schoolboy knows that if you take a twig and peel it there is a green layer underneath which the botanist calls concealed chlorophyll. I was wandering across Hampstead Heath one spring morning, and I asked myself, "How are these things coming into life in a week or two?" and I pulled off what lay above the so-called concealed chlorophyll and held it up to the sun. There was quite a lot of light streaming through it. It was a beautiful colour-screen which was inhibiting those rays which were obnoxious to the plant, which would prevent its growth or kill it, and letting through exactly the ones that it wanted for its photosynthetic work. If you imagine in February or March that you are a wizard out in the woods and say, " Hey, Presto ! Get clear of all this thin layer of bark," you would have a green wood in front of you like in the springtime, and that greenness is not concealed; it is only veiled, as I will show you at the end of the lecture. It is that light which causes the life to come on land, and in very much the same kind of way in the sea, except that there is not so much of the critical angle effect described above for the sea, but there is a good deal of absorption of light upon land because of the much greater length of atmosphere traversed before the rays reach the plants.

Let me put it in this way. As the Autumn goes on towards Christmas each day gets shorter. Light grows feebler all the time, and what physiologists call catabolic processes (oxidations) in the plant prevail over the anabolic processes (reductions). Then Christmas is passed, and the longer days come; more light pours in, and the situation then turns round the other way. In the November and December months more carbon dioxide is formed by the plant than corresponds with the carbon absorbed as organic compounds. The plant was living on past stores, but as March and April approach, all the time beneath that thin film of bark, especially on the smaller twigs, there is this layer of chlorophyll. It is working away all the time, and reduction outpaces oxidation, a plethora of stored organic matter rapidly accumulates, and finally the buds break out. If you look at the size of these things in the spring—observe a tree like a horse-chestnut in bud—you will see that the amount of stuff produced is enormous. It could not possibly come from reserve stores. The explanation is simply that before the green leaf, the most excellent form for producing and building up organic things, comes out, its birth is heralded by something which is going on underneath the bark in this so-called concealed chlorophyll, which really is not a concealed chlorophyll at all.

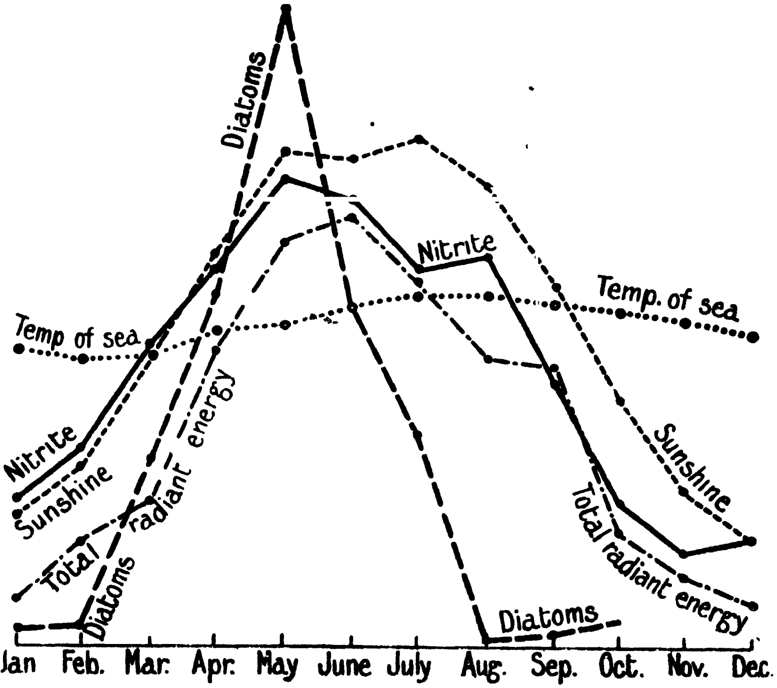
Just lately I went out with Mr. Edward Whitley to Geneva to study the flora of Lake Leman there. We went in search of an alga that is supposed not to contain chlorophyll and yet can synthesise. It is supposed to live at the bottom of the lake. Professor Emil André * took us out in his motor yacht and we got this stuff. We found it was only a thin film of material that really was not organic at all. It was chiefly dead diatoms, and other debris that had fallen down through the lake. We felt rather hopeless at having gone all that way and got nothing, and we discarded the yacht and went out in a little rowing boat. We made a

* Professor of Lacustrine Zoology, University of Geneva

discovery which really has been rejoicing me ever since. I have told you that if you expose marine algæ to light, the solution in which they are exposed turns alkaline, because they build up the carbon dioxide and turn out the alkaline carbonates. After we had discovered that fact, I asked Whitley to continue the investigation at Oxford. He drew a complete negative. He could not get any alkalinity as evidence of photosynthesis in any of the fresh-water plants then used. We really could not understand the matter a bit—why we should get it in the sea and not get it in the fresh-water. Having been disappointed at Geneva, we turned round to try a whole series of these fresh-water plants from Lac Leman to discover whether they would go alkaline or not, and what we found out as the result was that the fresh-water alga behaves like the marine alga, but that the higher fresh-water plant does not. It photosynthesises. It builds up nitrogen, but it does not give any alkali out to the surrounding medium in which it is growing. That is quite an interesting fact in itself, but if you think a little longer about it the interest increases, because it was only when that sort of semipermeable membrane for alkali established itself that it was possible for anything to emerge from the water and step ashore on to dry land. Any of the terrestrial plants, a tree or an herb or a blade of grass, cannot part with alkali. It cannot behave like a marine alga in the sea and take in bicarbonate and give out carbonate again. It must depend on what it takes up from its rootlets. It must have a supply of alkali in its own substance, and as the sunlight plays upon it it must take in *free* carbon dioxide from the atmosphere, and keep on all the time, using over and over again that same supply of alkali that it possesses. In other words, it must possess a regulation of alkalinity. It is the rudimentary trace of that preservation of alkalinity which runs right up to man from this point at the beginning of organised beings.

In order that animals can flourish on the land, and in order that the whole terrestrial civilisation can arise, there must develop a system by which the land plant takes its alkali up from the root, retains this store of alkali, and simply takes in free carbon dioxide and utilises its alkali over and over again to form bicarbonate on which the sunlight plays and produces organic matter. The point—and rather a beautiful point—is that all this evolution happened in the fresh water before the plants emerged. Above the algal level that new order of things does establish itself, and the higher aquatic plant in fresh-water resorts to terrestrial habits, and establishes this condition of affairs, then it can emerge and all terrestrial life commences. It is one of the earliest of these adjustments. Of course, physiologists know other fundamental adjustments at different levels. For example, at a certain stage in the evolution of fishes there was such an adjustment of the salt level. The great majority of the fish that are in the sea, including all edible fish, are not any salter than fresh-water fish. They develop what is called a certain " tonicity " in their blood, and that saline adjustment, once it has been established, persists right up to man through all the intervening species. In the same way, we get an adjustment of respiration. You can kill a mammal if you over-breathe it. In my opinion, a great deal of the evil effects of what was called " shock " during the war, and is called " shock " still by the surgeon, is due to a variation in the adjustment of that degree of alkalinity. Here then, right down at the algal level, we find now the very first traces of the adjustment of the reaction, and of a condition of affairs which makes it possible for life to emerge on the land.

FIG. 2.

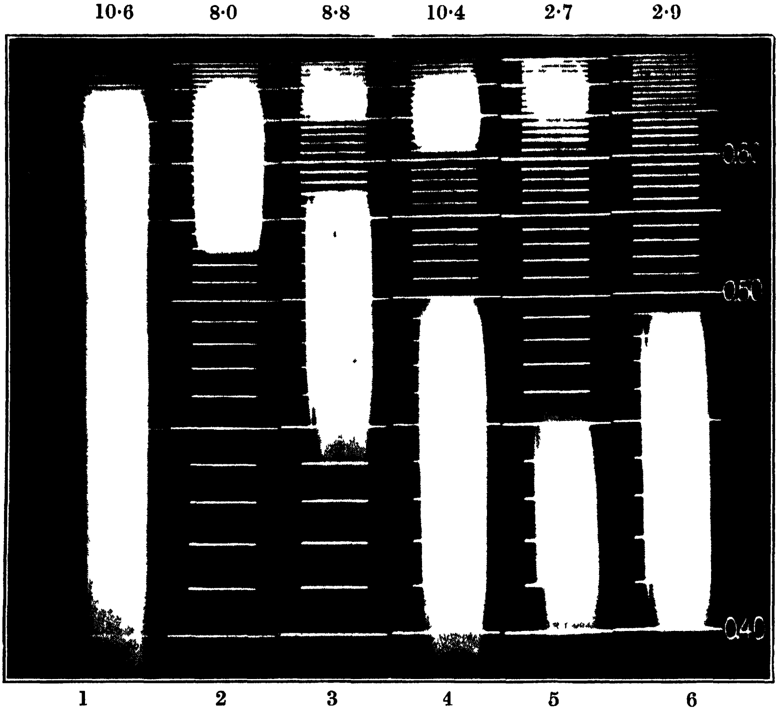


Now I will turn to some of my lantern slides, and show you the figures in support of what I have been saying.

Figure 2.—Here there is represented a compilation of a series of different data. I cannot claim credit that any line of the series

of data belongs to myself. All I can claim is that I correlated them. On the base-line you see marked out the months of the year. Then there are several curves above the base-line which are plotted to different scales. They are so plotted as to bring them together so that you can study them. The units used in plotting do not particularly matter and need not now be described. The point is not exactly how the curves rise, but the interest rather lies in how they follow one another. You will see there is one curve that does not follow the others, and that is the temperature of the sea at Port Erin, Isle of Man, over an average of ten years. We come next to the diatoms in the sea on which the life of the fishes depends. Observe that in February there are very few diatoms. The light, remember, is increasing all the time, and between February and March you see how they increase and get to their maximum about April. Then the light gets too strong for them and they come down again, and in the winter months after August they come quite low down. Look next at the sunshine curve following so closely the numbers of diatoms. Another curve shown there is the total radiant energy. The curve showing "nitrite" is the average amount for the last fifty years at Radcliffe Observatory, Oxford, of what used to be called "ozone." There is not any ozone on the surface of the earth. The substance present and formerly taken for ozone is nitrogen trioxide, and it is quite interesting to speculate as to what that means in the air at the surface of the earth. It was supposed that the nitrites and nitrates in the air were derived from thunderstorms. There is not the least evidence at all to support this view. You can take the rain that falls after a thunderstorm and you will find no more nitrite in it than you will find in an ordinary shower. The amount present at any given time does not follow the amount of electric disturbances in the air, and you can see by the diagram, on the other hand, how very closely it does follow the sunshine. That is quite an interesting point, because plants take up these nitrites from the air and nourish themselves from it, and there is a considerable amount of direct nutrition of plants accomplished in that way by the simple taking up of nitrites. I think also it is worth the while of the chemist to look into the matter from the point of view as to how accumulations of nitrites occur on the earth's surface. Such deposits are usually found in Peru and India, where there is so little rain to begin with, where there is intense sunlight, and where there probably is some supply of alkali to fix the nitrogen trioxide, because we do not find it as acid, but as the salts, sodium nitrate and sodium nitrite. Another important photosynthetic reaction is that by which nitrates pass over into nitrites. To carry it out you want

Fig 3.



This series of spectrograms, and the figures for alkalinity developed as shown over each spectrum, illustrate the photo-synthetic activity of each part of the solar spectrum, and demonstrate that all regions are utilisable and not merely the regions of the absorption bands of chlorophyll. It is also to be noted, as described in the text, that the longer wave-lengths in red, yellow, and green are the most active. From left to right the coloured screens are to the eye: No. 1, full spectrum; No. 2, red screen; No. 3, green screen; No. 4, yellow screen; Nos. 5 and 6, blue and violet screens.

My thanks are due to Mr. J. E. Barnard, late President of the Royal Microscopical Society, for taking these spectrograms for me.

[*To face Trans.*, *p.* 1565.

nothing more elaborate than an ordinary soup plate, putting into it a solution of one part in ten thousand of sodium nitrate, exposing it for an hour or two to such sunshine as we are having at present, and you will get an intense reaction, showing that nitrite is developed. That reaction means the uptake of energy. The number of these endothermic reactions that we have hitherto discovered is very small. The one in the green cell is the most predominant of all, but a similar reaction occurs between nitrates and nitrites with uptake of the energy of the light. That is without a green cell at all. In the presence of a green cell you get a fixation in the form of protein of amino-nitrogen from the atmosphere when you have no nitrate whatever present. That has been disputed for about one hundred and fifty years, but after a good deal of work I have not the remotest doubt that both the lower and higher plants do build up nitrites and nitrates and form organic nitrogenous compounds from the free nitrogen of the atmosphere. Those are the main points about that diagram. What I want to point out is that the outburst of Spring has not much to do with the temperature of the sea, but it has a great deal to do with the amount of sunshine. A great deal of our life, unconsciously to us, is bounded by sunshine. Many unhealthy lives are produced by the lack of sunshine. If you get either too much or too little sunshine, there is ill-health over the whole world. We do not realise at all to what extent we are dependent on a properly modulated amount of sunshine throughout the year.

Figure 3.—This is an experiment showing to what extent different regions of the spectrum take a part in photosynthesis. You see the spectrum under a plain glass under sunlight only showing 10·6 c.c. of alkalinity * after a given exposure. Then we get 8 c.c. with that simple bit of reddish-yellow light shown in the second spectrum alone remaining for photosynthetic action. In the fourth one there is almost as much, namely, 10·4 c.c., as in the full sunshine, although all the intermediate parts of the spectrum are shut out. The next two show how poor the blue light is in producing photosynthesis, the amounts being 2·7 and 2·9; this is, of course, quite different from the photographic plate. There are two things shown by this set of spectra and their accompanying figures. First of all, that it is not merely in the region of the absorption bands of chlorophyll that photosynthesis occurs, but all throughout the spectrum. And secondly, that there has been evolved in the living green cell a mechanism, contrary to those

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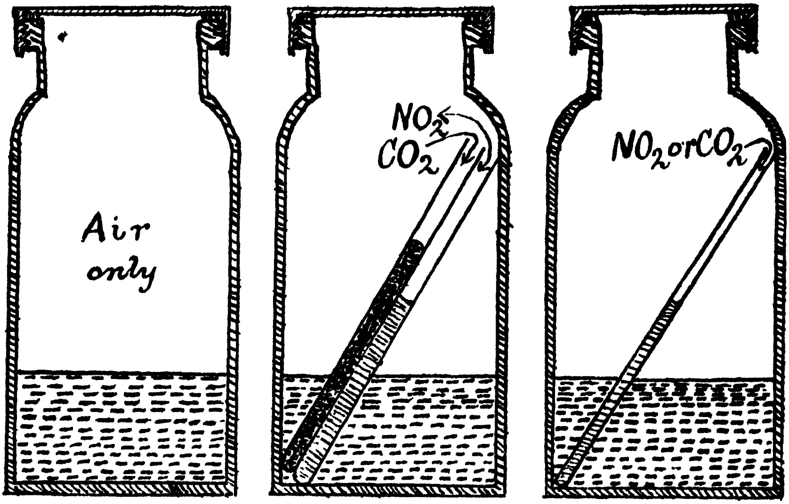
* That is, when 10 c.c. of sea-water in which the alga has grown are titrated with $N/100$-sodium hydroxide. The time of exposure was about five hours in all cases.

utilised in the beginning of organic things and to those affecting our photographic plates and ordinary chemical processes, a mechanism dealing with lower wave-lengths, and one which has to protect itself, by its colour screen, from the blue and ultra-violet, or else it gets killed.

Figure 4.—This experiment shows how growth may be stimulated by adding artificially oxides of nitrogen or sodium bicarbonate. What I did was to take a closed jar with a screw-down top and then in some cases put slanting side-tubes in, leaning against the wall of the jar. In some cases no tubes were inserted and in others simply a little solid sodium bicarbonate, in others a system which would slowly evolve nitrogen trioxide and in still others tubes which would evolve both gases. You see the amount of fixation of nitrogen in each case. With no additions at all, with the vessel quite closed up, one gets almost 4 milligrams of fixation of nitrogen. A small figure, you may say, but it is no smaller than that on which previous observers depend for all proof of the nitrogen-fixing bacteria and azotobacter. Then, if you put in some sodium bicarbonate you get an increase in the figure from 3·46 to 5·4; that is to say, the small partial pressure of carbon

Fig. 4.



To illustrate arrangement of screwed-down jars to show fixation of nitrogen and carbon. Similar arrangements can be made to demonstrate the nutrition of algæ from methyl alcohol, formaldehyde, and other poisonous simple organic substances. The nutrition tubes must be so narrow that the algal cells can utilise the poisonous nutrients as rapidly as they are evolved.

dioxide coming back from the sodium bicarbonate took the place of the carbon dioxide of the air which got exhausted in the jar when it was closed, and if you supply the sodium bicarbonate so that you get carbon dioxide coming out of the side tube, then at once this increase in fixation of carbon commences. I simply put a very narrow piece of glass tube drawn out like a test-tube into the sealed jar, with either one tube of sodium bicarbonate, or two tubes, one containing sodium bicarbonate and the other a little nitrite and very dilute acid to give off a small amount of nitrogen peroxide. You see the effect when you supply both. That is what manures do. They provide that stimulus at a certain period when the young plant wants it, to produce more rapid and enforced growth. They are stimulants similar to what physiologists call accessory food-stuffs. They carry the plant on through a certain stage, and I think that is the main purpose of manures and not direct building into the plant. The weight of rich manures supplied is many times smaller than the increase in the crop. Manures remove certain limiting factors of growth.

	Nitrogen fixed.
Nos. 1 and 2 (no additions)	3·46 mg.
Nos. 3 and 4 (sodium bicarbonate only)	5·40 ,,
Nos. 5 and 6 (oxides of nitrogen only)	2·50 ,,
Nos. 7 and 8 (both sodium bicarbonate and oxides of nitrogen)	14·10 ,,

ENDOTHERMIC FORMATION OF NITRITES FROM NITRATES.

The amounts of heat involved and differences in transition from one oxide of nitrogen to another are shown in the following table given by Mendeléeff, in which the numbers in the upper row represent thousands of gram-calories for a gram-molecular formation from the elements; and the lower shows in thousands of gram-calories the heats of transition from one oxide to the other:

$$\begin{array}{ccccccccc} N_2O & & N_2O_2 & & N_2O_3 & & N_2O_4 & & N_2O_5 \\ -21 & & -43 & & -22 & & -5 & & -1 \\ & -22 & & +21 & & +17 & & +4 & \end{array}$$

This table shows that in passage from N_2O_5 to N_2O_3, a supply of energy must be given to the reacting system amounting to $4 + 17 = 21$ thousands of gram-calories for each gram-molecule converted.

This table shows that there is an endothermic effect or absorption of light energy in the building up of the nitrogen trioxide.

The top line shows the amount of energy. If you take nitrate —*this* extreme right side—and pass that into N_2O_3; that is to say, from nitrate to nitrite—and the sun does that for you—there are 21 kilo-calories per gram-molecular weight going from HNO_3 to HNO_2. This is a very considerable accumulation of energy and it is going on all the time wherever nitrates are exposed to sunlight. We have known for a very long time the same thing about carbon. We have only recently acquired the same knowledge about nitrogen. If you get the inactive nitrates coming up from the soil into the leaf and being exposed to the sun, that action proceeds with the uptake of energy, and these nitrites are ever so much more active physiologically than are the nitrates, and that is the beginning, in my estimation, of the formation of the proteins in the plant—that you first of all get your nitrates to your nitrites. Ordinary running water as it comes down, or dew, contains these nitrites. If you allow water to stand for a day or two in the dark, or in a cistern or reservoir, or take it from an ordinary tap, you get no nitrite; but you have only to take that tap water, or water that has stood for some time, and put it in a soup plate in the face of the sun for two or three hours, and you get your reaction of nitrite at once. An endothermic reaction takes place and the nitrite is formed from a nitrate.

Fixation of Nitrogen by Marine Algæ.

CONDITIONS OF EXPOSURE TO LIGHT.

Exposures.

Nos. 1 and 2.—Kept with lids tightly screwed on in such daylight and sunlight as were available outdoors.

Nos. 3 and 4.—Ditto, but instead of tightly screwed-on lids, these were covered above only with a double layer of muslin, so that there was free access of atmosphere.

Nos. 5 and 6.—Exposed to diffuse light only indoors on shelf in laboratory, with lids tightly screwed on.

Nos. 7 and 8.—The same as to light, but open, with muslin covers only.

Nos. 9 and 10.—Kept in complete darkness in cupboard with lids tightly screwed on.

Nos. 11 and 12.—Also kept in darkness in cupboard with muslin covers only.

Results.

Experiment of March 28th—April 5th, 1919 *(seven days' interval).*

1.	2.		3.	4.	5.
Nature of exposure.	Daily titration in c.c. of *N*/100-acid in 100 c.c. of sea-water required to neutralise to phenolphthalein on the dates given.		Wet weight at end. Initial weight in each case, 2 grams in 800 c.c. of sea-water.	Dry weight at end. Gram.	Total nitrogen by Kjeldahl. In mg. for entire material.
	April 2.	April 5.			
1. Sunlight, in *shut* jars, outdoors	13·3	9·7	2·57	0·476	11·3
2. Sunlight, in *open* jars, outdoors	6·7	9·7	2·38	0·457	12·4
3. Diffuse light, no direct sun, on shelf indoors. Shut jar	0·4	3·4	1·71	0·284	8·7
4. Same exposure as No. 3, but jars open	0·0	+1·7	1·47	0·285	8·0
5. Darkness, in cupboard. Shut jars	−1·7	−1·4	1·45	0·259	9·4
6. Same as 5, but jar open	−1·2	−0·3	1·50	0·275	9·5

NOTE.—At the end the contents of each pair of similarly exposed jars were united for purposes of analysis so that No. 1 in "Results" corresponds to Nos. 1 and 2 in "Exposures," No. 2 in "Results" to Nos. 3 and 4 in "Exposures," and so on.

These results show the fixation of nitrogen by marine algæ. Nos. 1 and 2 were exposed to sunlight. No. 1 was in a closed jar, and No. 2 was in an open jar. Nos. 3 and 4 were in a diffused light. Nos. 5 and 6 were kept in darkness. The jars in light were exposed for five days with fair sunshine, not nearly so intense as we are enjoying at present. You see how the wet weights run up and down in light or dark. They were all 2 grams to start with, and you see how the ones in the sunlight have gone up, and the others down, although the jars were shut in several cases. Next there is the dry weight, which shows a similar condition of affairs, and then there is the total nitrogen estimated by the Kjeldahl method. Fixation of nitrogen takes place without any appearance whatever of the production of bacteria. They remained perfectly clear, and to fix that amount of nitrogen by the azotobacter the amount of turbidity would be unmistakable. All observers on such bacteria state that their media became turbid or milky. These algal growths do not get milky. I do not want to pursue that argument too far, but it seems to me that it is intensely interesting—whether it is done by two things working together, one of which is a bacterium, or by the green cell alone. Suppose we grant there are bacteria. There is an association of the two things together. There is a process instituted by which an energy transformer can take hold of sunlight, and by means of that sunlight capture the nitrogen of the atmosphere and convert it into proteins. That is far more important than worrying ourselves as to whether it is done by the green plant alone, or by the green plant plus some bacterial agency.

The table given below shows in similar fashion the fixation of nitrogen by fresh-water algæ. The organisms were simply sewn into each jar in fresh-water.

In order to save space in tabulation the amounts of nitrogen found by the Kjeldahl determination carried out at the conclusion of the experiments are here placed opposite the description of the treatment of each jar:

No. 1.—Tap-water and algæ only, glass lid screwed down, kept in light. N = 0·3 mg.

No. 2.—Tap-water and algæ only, no glass lid, top covered by fine lawn, kept in light. N = 1·6 mg.

No. 3.—Tap-water and algæ only, screwed down, no glass lid, kept in darkness. N = 0·1 mg.

No. 4.—Tap-water and algæ only, covered by fine lawn, kept in darkness. N = 0·3 mg.

No. 5.—Tap-water, algæ, 2 c.c. of 5 per cent. $Na_2HPO_4,12H_2O$ (that is, 0·05 per cent. of $Na_2HPO_4,12H_2O$), lawn cover only, kept in light. N = 8·1 mg.

No. 6.—Tap-water, algæ, 0·05 per cent. of Na_2HPO_4, screwed down glass lid, kept in light. N = 1·0 mg.

No. 7.—Tap-water, algæ, 0·05 per cent. of Na_2HPO_4, 0·05 per cent. of $NaNO_2$, lawn cover only, kept in light. N = 12·3 mg.

No. 8.—Tap-water, algæ, 0·05 per cent. of Na_2HPO_4, 0·05 per cent. of $NaNO_2$, screwed down glass lid, kept in light. N = 0·7 mg.

No. 9.—Tap-water, algæ, 0·05 per cent. of Na_2HPO_4, 0·05 per cent. of $NaNO_2$, formaldehyde vapour at high dilution supplied from side-tube as described below, glass lid screwed down, kept in light. N = 3·8 mg.

No. 10.—Tap-water, algæ, 0·05 per cent. of Na_2HPO_4, no $NaNO_2$, formaldehyde vapour, glass lid screwed down, kept in light. N = 1·0 mg.

No. 11.—Tap-water, algæ, 0·05 per cent. of Na_2HPO_4, 0·05 per cent. of $NaNO_2$, dilute methyl alcohol vapour supplied from side-tube, glass lid screwed down, kept in light. N = 7·4 mg.

No. 12.—Tap-water, algæ, 0·05 per cent. of Na_2HPO_4, no $NaNO_2$, dilute methyl alcohol vapour from side-tube, glass lid screwed down, kept in light. N = 1·1 mg.

It is observable from the particulars given for assimilated nitrogen that this occurs even when no nitrogen is supplied. Any nitrogen supplied from without is returned and more with it, but even in those cases where none is supplied to the plants they still grow and fix organic carbon and nitrogen. Another quite interesting point shown in that experiment is that you can use things which are very poisonous to plants to supply them with food, if only you conduct the thing in the proper way. There has been a long-continued dispute over von Beyer's hypothesis that formaldehyde is the first substance formed in the photosynthesis in the way of carbon compounds, and observers have put formaldehyde, in various concentrations, into solutions, and usually they found that it killed the plant cells. On the other hand, if you take extracts of chlorophyll from plant tissues and expose them to the light they form formaldehyde themselves. These processes are reversive. The way to get at the thing with some success is not to put the formaldehyde or these other poisonous things into the solution, but to use a side-tube such as has been sketched above (Fig. 4, p. 1566). You just put your ordinary medium down with the materials in it, and place in the side tube formaldehyde in a dilute condition. Then you get the effects observed in the table given above, Nos. 9, 10, 11, 12. The nitrogen gets fixed. The formaldehyde is built into carbohydrates, fats, proteins, and other materials. This occurs only with a certain intensity of light. The germicidal action of sunlight may simply be a reversal of that process. If you take a green cell and expose it to ultra-violet light, you have to expose for a very long time before it is injured. If you take a thing like a tubercle bacillus—in fact, any colourless bacteria—and expose it, you will kill it in a minute or two. The poison may not be formaldehyde alone, for it is remarkable how organic compounds and living organisms disintegrate under the action of light, forming simpler and lethal substances. If you can imagine the living cell being invaded by formaldehyde produced by the action of light, you can readily see how it can be killed. All things in Nature are reversive. The world does not always go in the same direction. One time it is building up, and another time breaking down, just like the coming of the Summer and the Winter, and all the cycles that occur in Nature. Take such things as the heart-beat. It contracts; that is its period of activity. It relaxes; it carries out exactly the reverse process. Everything in Nature is phasic, and it is as a result of that phasic variation that we are able to progress in evolution and build up from one thing to another. Take all the pools round the coast. In winter they are acid. As the spring goes on they get more and more alkaline. You see the possibility that is expressed there for producing natural variations. One pool may be considerably more alkaline than another, and some new birth of creature may arise in it simply because its reaction is entirely changed. It is only due to the conservative processes of Nature that we do not get a series of weird races and things arising to every change of environment. Nature millions of years ago invented methods by which the reactions of our bodies, the fluids of our own bodies, are kept within excessively narrow limits, and it is probable to my mind that it may be variations outside those limits occurring in these ways which cause new species of creatures to arise. There is all the time a stability. I want to impress that as the key-note of the whole thing. The pot seems to boil over, so that from a position of extreme instability it passes once more over into a position where it is stable and can begin to make a new movement forward. It goes up from the electron right into our social relations of the present time. We all know how the pot is boiling now. We do not know what is going to happen to the pot, but even at the level of sociology there is this same principle going right through that starts out at the beginning. Evolution has its periods of activity and its periods of rest, and I am quite certain that it was nothing fortuitous whatever that brought life to this world, and that given the same train of chemical and physical events in any other part of the universe, I will not say that human beings may have arisen, but the same changes and complexities must absolutely have arisen. There must be thousands of worlds in which there is some form of life, some form of activity comparable to our life, and intrinsically in its essence the same as our life.

BIBLIOGRAPHY.

Part of this lecture relates to matters which have not been published before, such as the sudden outburst of Spring on land and sea, and the transparency of the screen overlying chlorophyll under the twigs before the new leaves appear. The remainder has chiefly been recorded in the *Proceedings* of the Royal Society during the past ten years. The whole has been drawn together in a volume recently published by Mr. Edward Arnold entitled "Biochemistry, a Study of the Origin, Reactions, and Equilibria of Living Matter." An earlier account will be found in a volume in the Home University Library on "The Origin and Nature of Life."

CLXXXIII.—*The* ortho-*Dimethylanthraquinones and their Derivatives.*

By ARTHUR FAIRBOURNE.

THE original reason put forward in favour of the accepted or 2 : 3 structure for the only previously known *o*-dimethylanthraquinone, and for its derivatives, was based on analogy showing the improbability of formation of the 1 : 2-dimethyl isomeride during the dehydration of *o*-3 : 4-dimethylbenzoylbenzoic acid (Elbs and Eurich, *Ber.*, 1887, **20**, 1361; Elbs, *J. pr. Chem.*, 1890, [ii], **41**, 6), an argument still held to be valuable (Barnett, "Anthracene and Anthraquinone," 1921, 33). Before the war, however, the author, who was then working with Dr. Weizmann in Manchester University, succeeded in separating a product from this particular dehydration which was quite unlike the quinone described in the literature, but which gave evidence, nevertheless, of capability of bromination and of oxidation to an *o*-dicarboxylic acid.

It appeared probable, therefore, in spite of the arguments previously put forward against the likelihood of its being produced, that this was the unknown 1 : 2-dimethylanthraquinone, or, alternatively, that it was the 2 : 3-dimethylquinone, and that the substance hitherto accepted as having the 2 : 3 structure was in reality either of a different constitution, in common with all substances derived from or connected with it, or was a mixture of the 1 : 2 and the 2 : 3 isomeric forms.

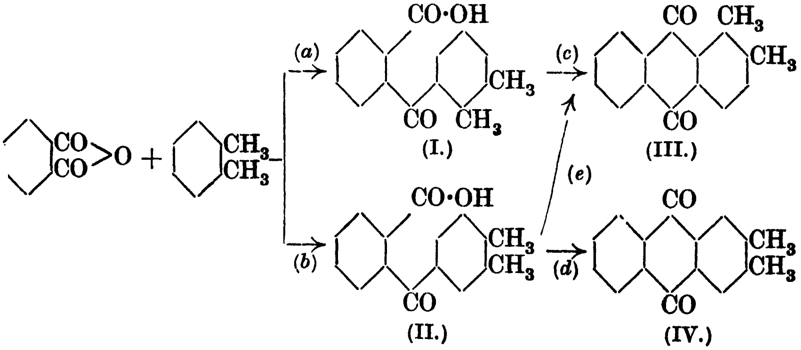
In the event of its being a mixture of this kind (compare variations of more than twenty degrees in the melting points of the specimens described by Elbs and Eurich and by various other experimenters; Limpricht, *Annalen*, 1900, **312**, 99; Willgerodt and Maffezzoli, *J. pr. Chem.*, 1910, [ii], **82**, 205; Heller, *Ber.*, 1910, **43**, 2890), then the additional evidence for the accepted 2 : 3 structure of all these substances which has arisen (Barnett) from the dissimilarity of the corresponding dicarboxylic acid, m. p. 340°, obtained by the oxidation of this dimethylquinone (Elbs and Eurich), with that obtained from other sources (Scholl and Swinger, *Ber.*, 1911, **44**, 2992), m. p. 268°, and undoubtedly having the 1 : 2 structure, is rendered uncertain, since the former acid of high m. p. obtained by Elbs may have come from either constituent of the isomeric mixture on oxidation, a possibility independently indicated by the fact that the latest worker (Heller) finds that this acid, made by the method of Elbs and Eurich, but obtained in a purer condition, does not melt at 340°, the temperature they state.

Moreover, the only remaining argument in favour of the 2 : 3 structure for all these substances (Elbs and Eurich) is that on reduction a dimethylanthracene has been produced, whilst a substance with a methyl group in the position 1 would in all probability have given quite a different type of compound, owing to the simultaneous interaction of this methyl group with the reduced carbonyl group of the anthraquinone radicle; but this argument is also rendered invalid, since the specimen of dimethylanthracene obtained may, like the dicarboxylic acid just mentioned, have come from either constituent of the isomeric mixture used, especially as no good yield is claimed in the description of this experiment.

For some time after the conclusion of the war *o*-xylene was unobtainable, and the author wishes to take this opportunity of expressing his thanks to Professor Crossley for very kindly offering a large private supply of this pure chemical to enable the work to be restarted, and the problem of the structure of these materials to be solved.

Phthalic anhydride and *o*-xylene were allowed to react in the presence of aluminium chloride to give *o*-dimethylbenzoylbenzoic acid as usual, and this acid was then dehydrated in a manner similar to that used by previous experimenters, but both possible *o*-dimethylanthraquinones resulted, and each has successfully been isolated.

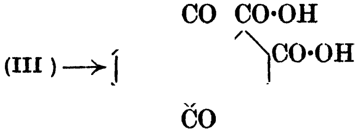
At first, in view of the published statements already referred to, that reaction (*e*) was very improbable, it might be supposed that



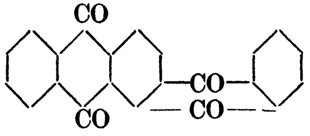
the isolation of both III and IV (although it was not known which product was represented by which formula) necessarily proved the existence both of I and II as requisite intermediate products in reactions (*a* and *c*) and (*b* and *d*) respectively; but subsequent careful fractional crystallisation of the sharply melting benzoylbenzoic acid used, and separate dehydrations of the successive crops of crystals obtained in this way from different solvents, have always yielded both quinones in quantity, whence the whole of the benzoylbenzoic acid used is proved to have the structure II, since I would be incapable of yielding IV by any reaction, a conclusion as to the structure of the acid which is in accordance with previous beliefs and proofs (Meyer, *Ber.*, 1882, **15**, 636).

From this proved constitution of the specimens of acid actually used in these particular experiments, it necessarily follows that products III and IV must have the constitutions here assigned to them, unless wandering of the methyl groups has occurred; and such wandering, moreover, does not take place during these reactions, for, as will be shown later, each of these isomerides oxidises to a corresponding *o*-dicarboxylic acid capable of forming an anhydride.

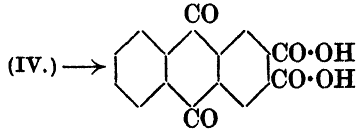
The proof as to which isomeride is represented by the 1 : 2- and which by the 2 : 3-dimethyl structure has been achieved by comparing these acids with the 1 : 2-dicarboxylic acid prepared by Scholl and Schwinger; and has then been independently confirmed by condensing both the 1 : 2- and the 2 : 3-anhydrides with benzene to give 1 : 2-phthaloylanthraquinone (VII) and dinaphthanthradiquinone (VIII) (compare Philippi, *Monatsh.*, 1911, **32**, 631; Scholl and Seer, *Annalen*, 1912, **394**, 159; Mills and Mills, T., 1912, **101**, 2194) respectively, thus :



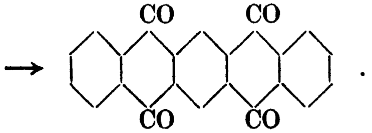
(V.) *Identified.*



(VII.)

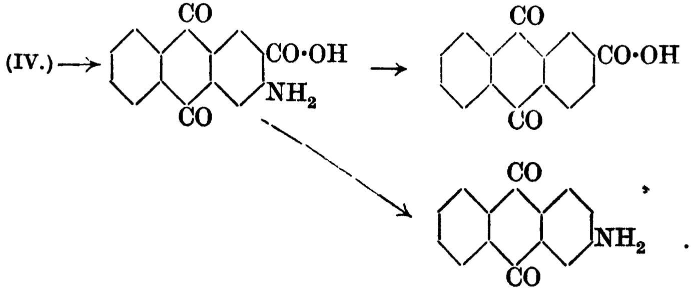


(VI.)



(VIII.) *Identified.*

As shown by the above formulæ, the established identity of these products* satisfactorily fixes the structure of all the materials involved, the quinone with m. p. 150° being therefore the 1 : 2-dimethylanthraquinone, and the other, m. p. 208°, the 2 : 3-dimethylquinone. Elbs and Eurich, whose quinone melted at 183°, must consequently have been dealing with a mixture of these two, and the specimens of higher m. p. described by Limpricht, m. p. 200°, and Heller, m. p. 205°, must also have been mixtures, but increasingly rich in the 2 : 3-dimethyl isomeride. Of these, only the specimen (m. p. 183°) of Elbs and Eurich was employed for supposed structural identification, and, as is now seen, it must certainly have contained the quinones of both possible *ortho*-structures in very considerable quantities, and it must, moreover, have given rise therefore to mixed derivatives belonging both to the 1 : 2 and the 2 : 3 series of substituted anthracene and anthraquinone products. Further, the quinone described by Willgerodt and Maffezzoli, and supposed by them to be the pure 2 : 3-dimethyl isomeride, which they used in their preparation of the dicarboxylic acid required for the attempted synthesis of the anthraquinone analogue of indigo, was almost certainly the same mixture as that used by Elbs and Eurich, since its preparation was stated to be identical with theirs, and since no difference was recorded between its properties and those which Elbs and Eurich had already described. This lack of evidence as to isomeric purity is doubly unfortunate in this particular case, in so far that not only are the constitutions of all the interesting substances synthesised thus rendered uncertain (for, from the details given, some at least, for example, the dicarboxylic acid and its anhydride, must have been mixtures), but, also, although it has never been so claimed, their work would have been an entirely successful determination of the structure of all these *ortho*-disubstituted anthraquinones now in doubt, had the isomeric purity of the initial dimethylquinone previously been assured; because from this dimethylquinone the dicarboxylic acid was prepared (m. p. not stated) and this was successfully converted into an anhydride, imide, half amide, and amino-acid, and the last compound was proved to have both its amino- and its carboxyl groups in β-positions by the elimination of each alternatively, leading to identifiable β-monosubstituted anthraquinones in both cases, thus :



A repetition of this work with either of the now separated isomerides has not, however, as yet been undertaken, owing to the previously mentioned method of determination of structure having offered less experimental difficulty, and having afforded, in addition, an independent confirmation of the structure of the second isomeride, and of its 1 : 2 series of derivatives, as already explained.

Anthracene- and anthraquinone-2 : 3-dicarboxylic acids, 2 : 3-dimethylanthracene and dimethylanthranol, the above-mentioned compounds of Willgerodt and Maffezzoli, and all substances connected with these, are examples of compounds the characterisation of which has suffered from the existence of this unsuspected 1 : 2-dimethyl isomeride in what has previously been accepted as the pure 2 : 3-quinone. Certain of these compounds have now been prepared isomerically pure, as described in the experimental portions of this paper, whilst others, and also many corresponding reactions in the 1 : 2-series, are at present under investigation by another member of this College.

EXPERIMENTAL.

o-3 : 4-*Dimethylbenzoylbenzoic Acid : Absence of its Isomeride.*

This was prepared by reaction (*a*), the method of Elbs and Eurich (*loc. cit.*; compare Limpricht, *loc. cit.*; Willgerodt and Maffezzoli, *loc. cit.*; Heller, *loc. cit.*), but after the acid had been obtained in a pure condition with a sharp melting point, it was, nevertheless, fractionally crystallised from chloroform, and also from acetic acid, many times, the various crops of crystals being then separately submitted to reactions (*c*) and (*d*) as described below. Since both these possible dehydrations always occurred simultaneously, yielding both III and IV in quantity from every fraction of acid used, all confusion due to the possible presence of *o*-2 : 3-dimethylbenzoylbenzoic acid (I) in the following experiments has been entirely eliminated, this isomeride being incapable of yielding IV under any conditions; and thus the arguments used in the theoretical and in subsequent portions of this paper have been justified, and any trouble which might otherwise have arisen owing to the possible presence of the *m*- or *p*-isomeride in the *o*-xylene has also been obviated.

1 : 2-*Dimethylanthraquinone* (III).

A mixture containing about 80 per cent. of the 2 : 3- and about 20 per cent. of the 1 : 2-isomeride was prepared by reactions (*c*) and (*d*) simultaneously from each of the fractions of the dimethylbenzoylbenzoic acid mentioned above, by a method similar to that used by Elbs and Eurich, and later investigators, for the preparation of the mixed quinones. One part of the benzoylbenzoic acid dissolved in 10 parts by weight of concentrated sulphuric acid was warmed gradually to 125° during half an hour, kept at this temperature for fifteen minutes, and then poured on ice. The precipitated light yellow powder was filtered, washed with water, sodium hydroxide solution, and again with water, and dried in a steam-oven. The dry powder, the yield of which was almost theoretical, was found to correspond with what previous experimenters have described as slightly impure 2 : 3-dimethylanthraquinone.

The 1 : 2-dimethylquinone was isolated from this mixture by taking advantage of the varying solubilities of the isomerides in acetic acid and acetone. A solution containing 12 c.c. of boiling glacial acetic acid for every gram of the isomeric mixture was filtered, allowed to cool, and kept during one hour. The crystals obtained were removed, and the mother-liquor was largely diluted with cold water, when a very pale powder separated. This was filtered off, washed with sodium hydroxide solution and water, dried, and crystallised from acetone several times. Quick crystallisation, caused by the addition of a small quantity of the pure material to the cooled, supersaturated solution, was used after this had once been obtained, and filtration was then carried out before crystallisation of the 2 : 3-isomeride had taken place. In some cases a final crystallisation from glacial acetic acid was also performed in order to leave the product in a state comparable with that of its isomeride in these experiments, but this had no effect on the properties of the washed and dried substance. From either solvent small clusters of nearly white needle crystals, m. p. 150°, were obtained, soluble in ether, alcohol, or benzene, and stable to alkalis and to hot alkaline potassium permanganate. A red coloration was produced, however, when this material was treated with ammonia and zinc dust (Found : $C = 81{\cdot}2$; $H = 5{\cdot}1$. Calc., $C = 81{\cdot}36$; $H = 5{\cdot}08$ per cent.). Its structure is proved by its method of formation and its oxidation to the 1 : 2-dicarboxylic acid described below, and is confirmed by the condensation of its 2 : 3-isomeride with benzene, as has been explained in the theoretical portion.

2 : 3-*Dimethylanthraquinone* (IV).

The isomerically pure 2 : 3-dimethylquinone was obtained from the crystals deposited during the first, or acetic acid, crystallisation referred to in the preceding preparation. These were recrystallised several times from fresh glacial acetic acid, then washed with water, and dried in an air-oven. With the exception of the higher melting point (208°) already referred to, the properties of this substance did not differ from those given by previous experimenters for the unseparated isomerides (Elbs and Eurich, *loc. cit.*; m. p. 183°) (Found: C = 81·3; H = 5·1. Calc., C = 81·36; H = 5·08 per cent.).

Anthraquinone-2 : 3-*dicarboxylic Acid and its Anhydride.*

The isomerically pure 2 : 3-dimethylanthraquinone was oxidised to the corresponding dicarboxylic acid in a manner similar to that by which Elbs and Eurich oxidised the mixed quinones. One part by weight of the pure quinone was heated with seven parts of diluted nitric acid (D 1·1) at 200° for six hours. The crystalline product was filtered, washed with water, and recrystallised from acetic acid. The crude product, the yield of which was almost theoretical, did not melt at 350° (compare Elbs, m. p. 340°). In its general properties it was in agreement with Elbs' dicarboxylic acid; no coloration was produced during solution in alkalis, however, unlike the specimen described by Elbs, which appears therefore also to have been a mixture of the two possible isomeric forms, as were the quinones from which it was made. The acid readily passed into an anhydride by treatment with acetic anhydride, or by fusion or sublimation. This did not melt at 300° (compare Elbs and Eurich, m. p. 290°), but otherwise its properties were similar to those of the anhydride previously described (Found for the acid: C = 64·7; H = 2·9. Calc., C = 64·86; H = 2·7 per cent. Found for the anhydride: C = 69·4; H = 2·5. Calc., C = 69·1; H = 2·2 per cent.).

A comparison of the properties of these substances, especially their high melting points, with those of the corresponding acid and its anhydride made from the 1 : 2-dimethylanthraquinone, as described immediately below, will be seen to prove this acid to be definitely the 2 : 3-dicarboxylic isomeride.

Anthraquinone-1 : 2-*dicarboxylic Acid and its Anhydride.*

The oxidation of the 1 : 2-dimethylanthraquinone to its corresponding dicarboxylic acid was identical in method with that used for its isomeride, except that a temperature ten degrees lower was found advisable. The yield was again very good, a mass of fine yellow needles resulting, which, when crystallised from water, melted at about 265°, and when treated with acetic anhydride precipitated the corresponding anhydride, m. p. 320° (approx.); and in other respects the properties agreed with the recorded descriptions of this substance (Badische Anilin- & Soda-Fabrik, Fr. Pat. 1910, 423986; Scholl and Schwinger, *Ber.*, 1911, **44**, 2992; Scholl, D.R.-P. 1911, 241624; 1911, 243077). Since all the specimens previously described have been prepared by the breaking of a benzene ring attached in the 1 : 2 positions to an anthraquinone radicle, there can be no doubt that the carboxyl groups, and the methyl groups of the *o*-dimethylanthraquinone from which it was prepared, are also in the 1 : 2 positions, as has already been explained.

Dinaphthanthradiquinone (VIII).

Dinaphthanthradiquinone (*lin.*-dibenz-1 : 4 : 5 : 8-anthradiquinone) has been successfully prepared from 2 : 3-dimethylanthraquinone, thus independently confirming its 2 : 3 structure. The anhydride (10 grams) of the dicarboxylic acid prepared as described above, was warmed with benzene (1 litre) and aluminium chloride (10 grams) until the reaction started, and the mixture was cautiously heated throughout the progress of the reaction until hydrogen chloride ceased to be evolved. The reddish-yellow product was treated with water and hydrochloric acid, and was extracted with further portions of benzene. These extracts were evaporated and to their residue was added a yellow solid which had remained undissolved during the extractions. This product was then purified by precipitation from solution as an ammonium salt, but this purification of the acid led to so much difficulty that it has not as yet been completed, although the crude acid obtained was sufficiently pure to be dehydrated. It was heated gradually in twenty parts by weight of concentrated sulphuric acid to 110°, and maintained at that temperature for ten minutes, after which the black solution was filtered through glass wool, and diluted largely with water. The precipitate was washed with sodium hydroxide solution, and with water, then with a little glacial acetic acid. It was recrystallised from fresh glacial acetic acid, and finally was sublimed, when golden-yellow needles, stable up to, and melting at, a little more than 400°, were obtained. Independent proof was thus afforded of the 2 : 3 positions of the carboxyl groups in this molecule, as dinaphthanthradiquinone has already been proved to have a linear constitution (Philippi, *loc. cit.*; Mills and Mills, *loc. cit.*; Scholl and Seer, *loc. cit.*) (Found: C = 78·4; H=2·9. Calc., C = 78·1; H = 2·96 per cent.).

1 : 2-*Phthaloylanthraquinone* (VII).

This substance was prepared in an exactly similar manner to that used in the case of its isomeride, the intermediate compound formed from the condensation of anthraquinone-1 : 2-dicarboxylic acid with excess of benzene in the presence of aluminium chloride again not being isolated, owing to the difficulties experienced in its attempted purification. The crude product of the condensation was therefore partly purified as an ammonium salt and then immediately dehydrated by treatment with twenty parts by weight of concentrated sulphuric acid at a temperature of 110° during twenty minutes. The black liquid which resulted was filtered through glass wool, and poured into water, when a dark solid separated. This was washed with water and with dilute sodium hydroxide solution, and, after being dried, was crystallised from glacial acetic acid and boiling nitrobenzene. 1 : 2-Phthaloylanthraquinone was thus obtained as a greenish-yellow, acicular, crystalline product which decomposed before a definite melting point could be taken. Sublimation has not been successful, and combustion indicates that the material was not quite pure (Found : C = 78·6; H = 2·8. Calc., C = 78·1; H = 2·96 per cent.).

2 : 3-*Dimethylanthracene.*

Pure 2 : 3-dimethylanthraquinone was reduced by the method of Elbs and Eurich, and the product was found closely to resemble the dimethylanthracene they describe (*Ber.*, 1887, **20**, 1361; *J. pr. Chem.*, 1890, [ii], **41**, 6), although the melting point was slightly higher, presumably owing to the absence of reduction products of the 1 : 2 series. This preparation of the anthracene from the purified 2 : 3-dimethylanthraquinone allows Elbs' argument as to the structure of these materials again to be applied as a probability, although the attempted reduction of the other isomeride has not as yet confirmed the formation of an inner ring such as is required by these considerations (Found : C = 92·9; H = 6·7. Calc., C = 93·2; H = 6·8 per cent.).

*Anthracene-*2 : 3-*dicarboxylic Acid.*

Pure anthraquinone-2 : 3-dicarboxylic acid was mixed with a large excess of zinc dust (six parts by weight) and dissolved in ammonia solution to which an equal volume of water had been added, 100 c.c. of this ammonia solution being used for every gram of the acid taken. The whole charge was then heated with constant shaking on the water-bath during two hours, when the pure anthracenedicarboxylic acid was precipitated from the hot filtered solution by the addition of hydrochloric acid, and was recrystallised from boiling alcohol. Small crystals were obtained which did not melt at 350°, but which were capable of sublimation to the anhydride as stated by Elbs

(Found: C = 71·9; H = 3·7. Calc., C = 72·2; H = 3·8 per cent.).

The o-*Dimethylanthranols and Other Reduction Products.*

Limpricht (*Annalen*, 1900, **312**, 99) reduced 3 : 4-dimethylbenzoylbenzoic acid to the corresponding dimethylbenzylbenzoic acid, and he then dehydrated this, obtaining the dimethylanthranol, which he classified as the 2 : 3-isomeride, giving as evidence that oxidation produced an *o*-dimethylanthraquinone, m. p. 200°. From experiments so far carried out it would appear, however, that, just as in the case of the dehydration of the benzoylated acid, in which both isomerides result, so also in the dehydration of the benzylated acid both possible isomerides again result, and that the compounds described by Limpricht, including the final quinone, were 1 : 2- and 2 : 3-dimethylated isomeric mixtures, particularly rich, however, in the 2 : 3-form. The attempted isolation of the substances belonging to the 1 : 2 series in these reactions, and also the reduction products of the members of this 1 : 2 series mentioned previously, are at present under investigation by another member of this College.

In conclusion, the author wishes to take this opportunity of expressing his appreciation of the interest taken by Professor Smiles in the arguments put forward in this paper.

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Strand, W.C.2

[*Received, July 22nd*, 1921.]

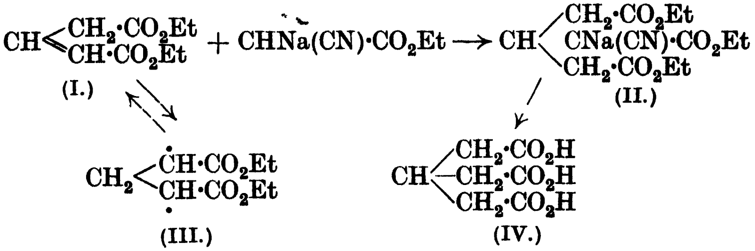
CLXXXIV.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part III. Conditions Controlling Synthesis by the Cyanoacetic Ester Method*—(continued).

By Christopher Kelk Ingold and Edward Arthur Perren.

The conditions which appear to govern the synthesis of the methanetriacetic acids by the interaction of ethyl sodiocyanoacetate either with halogen compounds or with the esters of unsaturated acids have been examined in some detail in a recent communication

(Part I, this vol., p. 341) and have been shown to be most intimately bound up with that peculiar molecular condition of which glutaconic acid affords the best known and most typical example. The present paper deals with another controlling factor of equal importance in the devising of such synthetical methods, and also of some general interest in so far as it is concerned with the reversibility, under certain conditions, of the Michael reaction.

At an early stage of the investigation just referred to it had become apparent that the difficulty attending the formation, for example, of the ester II (which on hydrolysis yields methanetriacetic acid, IV) by the condensation of ethyl sodiocyanoacetate with ethyl glutaconate (I) was to be ascribed to the fact that under customary experimental conditions ethyl glutaconate consists almost entirely of its "normal" modification (III). Such "normal" glutaconic acid derivatives do not behave as ordinary unsaturated compounds; they condense, for instance, with ethyl sodiocyanoacetate with great reluctance and in an abnormal manner, yielding products of 1 : 3-addition, as, indeed, the "semi-aromatic" mode of representation requires. Plainly, therefore, unless some special device be employed, such as utilising the unsaturated modification



$$CH\begin{cases}CH_2\cdot CO_2Et\\CH\cdot CO_2Et\end{cases} + CHNa(CN)\cdot CO_2Et \longrightarrow CH\begin{cases}CH_2\cdot CO_2Et\\CNa(CN)\cdot CO_2Et\\CH_2\cdot CO_2Et\end{cases}$$

(I.) (II.)

$$CH_2\begin{cases}\dot{C}H\cdot CO_2Et\\ \underset{\bullet}{C}H\cdot CO_2Et\end{cases} \qquad CH\begin{cases}CH_2\cdot CO_2H\\CH_2\cdot CO_2H\\CH_2\cdot CO_2H\end{cases}$$

(III.) (IV.)

of the glutaconic acid derivative in the nascent condition (this vol., p. 492), no condensation product of the required type can be expected, except from glutaconic acid derivatives the unsaturated forms of which are considerably more stable than that of glutaconic ester itself.

In the course of an extended series of researches Thorpe and his collaborators have shown that the presence of substituents in the α-position in derivatives of glutaconic acid increases the permanence of the unsaturated phase to a very notable degree; and it was for this reason that we decided to investigate certain esters of α-substituted glutaconic acids with respect to their capacity for entering into condensation with cyanoacetic ester.

The four substances which up to the present time have been examined in this connexion are ethyl α-carboxyglutaconate (ethyl *iso*aconitate) (V), ethyl αγ-dicarboxyglutaconate (VI), ethyl α-carboxy-γ-methylglutaconate (VII), and ethyl αγ-dicarboxy-α-methylglutaconate (VIII):

$$\mathrm{(CO_2Et)_2CH{\cdot}CH{:}CH{\cdot}CO_2Et} \qquad \mathrm{(CO_2Et)_2CH{\cdot}CH{:}C(CO_2Et)_2}$$

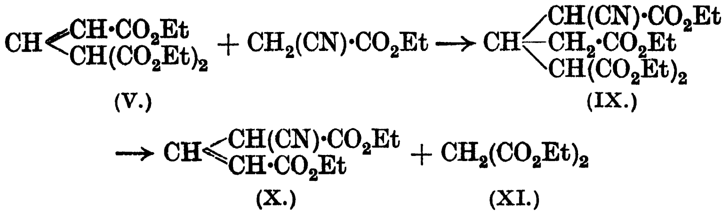
(V.) (VI.)

$$\mathrm{(CO_2Et)_2CH{\cdot}CH{:}CMe{\cdot}CO_2Et} \qquad \mathrm{(CO_2Et)_2CMe{\cdot}CH{:}C(CO_2Et)_2}$$

(VII.) (VIII.)

All these substances readily reacted with ethyl sodiocyanoacetate, and no evidence was obtained of their possessing any tendency to pass into their normal modifications (the ester VIII, clearly, has no normal form) under the experimental conditions employed. Nevertheless, the products of these condensations, excepting in one instance in special circumstances (p. 1586), contained no trace of the expected derivatives of methanetriacetic acid, but consisted almost wholly of fission products formed from these substances by a remarkable decomposition having the character of a retrograde Michael reaction.

The ester V, for instance, gave initially a condensation product (IX), which then underwent complete fission into ethyl α-cyanoglutaconate (X) and ethyl malonate (XI):



$$\mathrm{CH}{<}\begin{matrix}\mathrm{CH{\cdot}CO_2Et}\\ \mathrm{CH(CO_2Et)_2}\end{matrix} + \mathrm{CH_2(CN){\cdot}CO_2Et} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{CH_2{\cdot}CO_2Et}\\ \mathrm{CH(CO_2Et)_2}\end{matrix}$$

(V.) (IX.)

$$\longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{CH{\cdot}CO_2Et}\end{matrix} + \mathrm{CH_2(CO_2Et)_2}$$

(X.) (XI.)

The products were purified and identified with some considerable care, the ethyl malonate, for instance, by its boiling point, by analysis, and by conversion into malonamide. Ethyl α-cyanoglutaconate has been prepared both by Guthzeit and Eyssen (*J. pr. Chem.*, 1909, [ii], **80**, 41) and by Verkade (*K. Akad. Wetensch. Amsterdam*, 1919, **27**, 1132), whose descriptions closely agree with our own observations. The substance, however, was analysed and its identity fully confirmed by converting it into the crystalline ethyl derivative, $\mathrm{CO_2Et{\cdot}CH{:}CH{\cdot}CEt(CN){\cdot}CO_2Et}$ (XII), obtained by Guthzeit and Eyssen (*loc. cit.*, p. 44).

That the equations given above correctly represent the course of the reaction is, we believe, conclusively proved by the experiments described hereunder. In particular, the second reaction, involving as it does the elimination of ethyl malonate from a substance in which a number of substituted acetic acid residues are attached to the same carbon atom, is typical of the decompositions described in this paper; and it may be stated at once that the general character of the determining conditions, so far as we have been able to discover them, appears to be concerned with the accumulation at the same carbon atom of several branched-chain acetic acid residues, for, whenever this accumulation oversteps a certain limit, one of the groups, usually the largest, will be eliminated from the molecule.

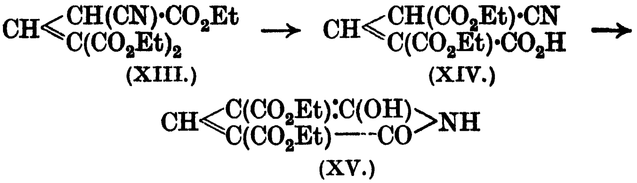
The ultimate cause of the reaction would therefore appear to be largely spatial in character and to be closely connected with the considerations recently put forward (this vol., p. 305, 951) relating to the distribution of groups of different volume around the methane carbon atom.

In extending the study of this reaction it was necessary in the first place to prove that it had some generality of application, and dicarboxyglutaconic ester (VI) was therefore investigated. This ester has one branched acetic acid chain more than ethyl *iso*aconitate, and there should be an opportunity for two separate ethyl malonate residues to become eliminated from the original condensation product with ethyl cyanoacetate. Moreover, from what has been said it will be anticipated that, in view of the presence of the additional branched chain, it might be possible to observe some tendency, at least, towards the elimination of *both* ethyl malonate residues from the molecule.

The main products obtained by the action of ethyl sodiocyanoacetate on ethyl dicarboxyglutaconate, or rather on its very stable sodio-derivative (Conrad and Guthzeit, *Ber.*, 1882, **15**, 284), were ethyl malonate and a yellow oil, which, although it could not be purified by distillation, gave on analysis figures approximating to those required for the cyanocarboxyglutaconic ester (XIII). In reality its principal constituent was this ester, which was separated in the pure condition by regeneration from its monosodio-derivative, a yellow, sparingly soluble substance very similar in all essential respects to the sodio-compound of ethyl dicarboxyglutaconate first prepared by Conrad and Guthzeit.

As an additional control on its constitution, the cyano-ester was subjected to regulated hydrolysis by hydrochloric acid, with which it reacted with extraordinary ease to form an acid cyano-ester (XIV). This, however, in the presence of the reagent, rapidly passed, by an internal rearrangement of a very familiar type (compare the formation of phthalimide from *o*-cyanobenzoic acid), into the well-known ester-imide of dicarboxyglutaconic acid (ethyl 6-hydroxy-2-keto-$\Delta^{3:5}$-dihydropyridine-3 : 5-dicarboxylate, a form of ethyl 2 : 6-dihydroxynicotinate, XV) (Guthzeit, *Ber.*, 1893,

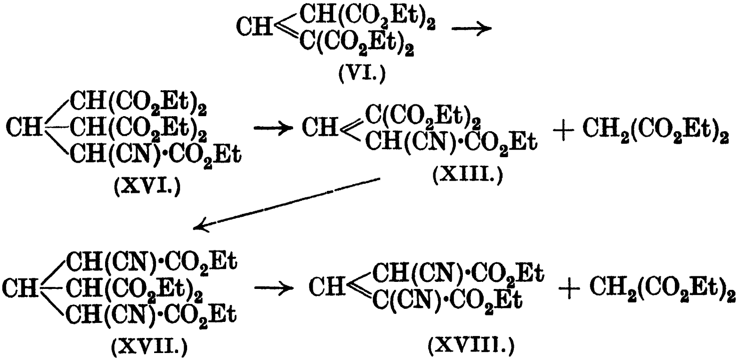
26, 2796; Errera, *Ber.*, 1898, **31**, 1243; Guthzeit and Eyssen, *loc. cit.*):



$$\underset{\text{(XIII.)}}{\mathrm{CH}\Big<\begin{array}{l}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{C(CO_2Et)_2}\end{array}} \longrightarrow \underset{\text{(XIV.)}}{\mathrm{CH}\Big<\begin{array}{l}\mathrm{CH(CO_2Et){\cdot}CN}\\ \mathrm{C(CO_2Et){\cdot}CO_2H}\end{array}} \longrightarrow$$

$$\underset{\text{(XV.)}}{\mathrm{CH}\Big<\begin{array}{l}\mathrm{C(CO_2Et){:}C(OH)}\\ \mathrm{C(CO_2Et)\text{——}CO}\end{array}\Big>\mathrm{NH}}$$

Besides ethyl α-cyano-γ-carboxyglutaconate and ethyl malonate, a small quantity of a crystalline material was isolated from the condensation product, and was identified as ethyl αγ-dicyanoglutaconate (Errera, *Gazzetta*, 1898, [ii], **27**, 393; Ruhemann and Browning, T., 1898, **65**, 280) (XVIII). The same substance was produced when ethyl cyanocarboxyglutaconate was treated with ethyl sodiocyanoacetate, and its formation in the original condensation must therefore have involved the production and subsequent fission of two methanetriacetic acid derivatives (XVI and XVII) by a series of direct and retrograde Michael condensations:



$$\underset{\text{(VI.)}}{\mathrm{CH}\Big<\begin{array}{l}\mathrm{CH(CO_2Et)_2}\\ \mathrm{C(CO_2Et)_2}\end{array}} \longrightarrow$$

$$\underset{\text{(XVI.)}}{\mathrm{CH}\left<\begin{array}{l}\mathrm{CH(CO_2Et)_2}\\ \mathrm{CH(CO_2Et)_2}\\ \mathrm{CH(CN){\cdot}CO_2Et}\end{array}\right.} \longrightarrow \underset{\text{(XIII.)}}{\mathrm{CH}\Big<\begin{array}{l}\mathrm{C(CO_2Et)_2}\\ \mathrm{CH(CN){\cdot}CO_2Et}\end{array}} + \mathrm{CH_2(CO_2Et)_2}$$

$$\swarrow$$

$$\underset{\text{(XVII.)}}{\mathrm{CH}\left<\begin{array}{l}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{CH(CO_2Et)_2}\\ \mathrm{CH(CN){\cdot}CO_2Et}\end{array}\right.} \longrightarrow \underset{\text{(XVIII.)}}{\mathrm{CH}\Big<\begin{array}{l}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{C(CN){\cdot}CO_2Et}\end{array}} + \mathrm{CH_2(CO_2Et)_2}$$

This therefore is a noteworthy extension of the reaction previously described. However, the yield of ethyl dicyanoglutaconate was never large * and it was not found possible to distinguish satisfactorily between the first and the second molecule of ethyl malonate eliminated during the successive fission reactions. Moreover, owing to the slight solubility in cold alcohol of the sodio-derivatives of ethyl cyanocarboxyglutaconate and ethyl dicarboxyglutaconate, it was impossible to conduct the series of changes at a low temperature (compare below); for this reason, and also because fractional distillation as a means of separating the products was impracticable, experiments on the isolation of the intermediate methanetriacetic acid derivatives met with no success.

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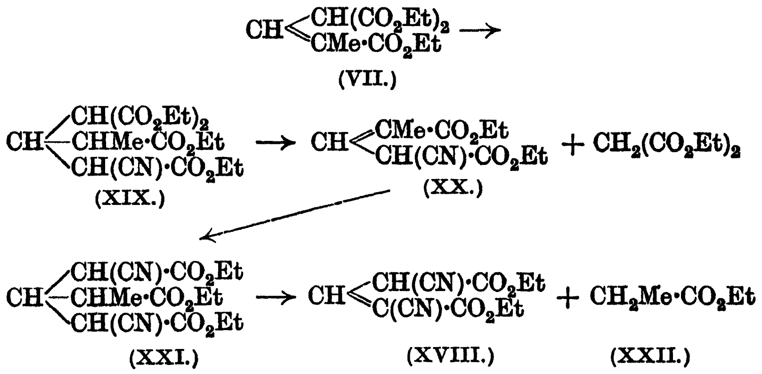
* Reference to two papers by Verkade (*K. Akad. Wetensch. Amsterdam*, 1915, **24**, 865; 1919, **27**, 1130) on ethyl cyanoglutaconate will suggest possible reasons for this.

Therefore we turned to another example, namely, that afforded by the condensation of ethyl α-cyano-γ-methylglutaconate (VII). Here the two substituted acetic acid residues, which, by analogy, one would expect to find as elimination products of the fission reactions, are not identical; one should be eliminated as ethyl malonate and the other as ethyl propionate, and by isolating and identifying these it should be possible to follow in detail the successive stages of the process. Actually, although the main products under the usual experimental conditions were ethyl α-cyano-γ-methylglutaconate (XX) and ethyl malonate, the quantity of ethyl dicyanoglutaconate (XVIII) produced was very considerable if the time allowed were prolonged; and, moreover, it was found possible in this case to separate and satisfactorily to identify ethyl propionate, the second of the eliminated residues. Further, by conducting the condensation at a low temperature, the later stages of the process became arrested to such a degree as to render practicable the isolation of the ω-methylmethanetriacetic acid derivative (XIX) originally formed. The complete series of changes is therefore as follows:



$$\mathrm{CH}{<}\begin{matrix}\mathrm{CH(CO_2Et)_2}\\ \mathrm{CMe{\cdot}CO_2Et}\end{matrix} \longrightarrow$$

(VII.)

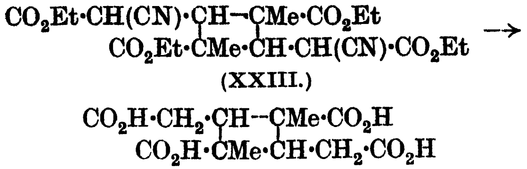
$$\mathrm{CH}{\lessgtr}\begin{matrix}\mathrm{CH(CO_2Et)_2}\\ \mathrm{CHMe{\cdot}CO_2Et}\\ \mathrm{CH(CN){\cdot}CO_2Et}\end{matrix} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CMe{\cdot}CO_2Et}\\ \mathrm{CH(CN){\cdot}CO_2Et}\end{matrix} + \mathrm{CH_2(CO_2Et)_2}$$

(XIX.) (XX.)

$$\mathrm{CH}{\lessgtr}\begin{matrix}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{CHMe{\cdot}CO_2Et}\\ \mathrm{CH(CN){\cdot}CO_2Et}\end{matrix} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{C(CN){\cdot}CO_2Et}\end{matrix} + \mathrm{CH_2Me{\cdot}CO_2Et}$$

(XXI.) (XVIII.) (XXII.)

Perhaps it should be added here that the course pursued by the condensation was in reality rather more complicated than this, owing to the extraordinary tendency possessed by the cyanomethylglutaconic ester to pass into a crystalline cyano-ester (m. p. 87°), which may provisionally be represented by the formula XXIII; for, on hydrolysis by means of acids, it yielded a tetrabasic acid (m. p. 242°), which, there is good reason to believe, is an acid (XXIV) belonging to the *cyclo*butane series:



$$\begin{array}{l} CO_2Et\cdot CH(CN)\cdot CH{-}CMe\cdot CO_2Et \\ \quad CO_2Et\cdot CMe\cdot CH\cdot CH(CN)\cdot CO_2Et \end{array} \longrightarrow$$

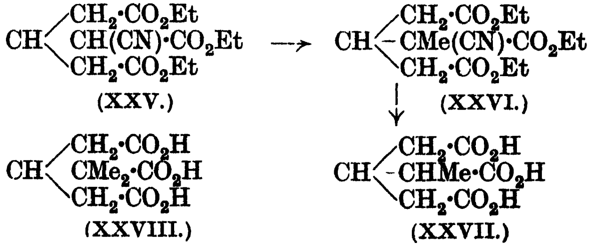
(XXIII.)

$$\begin{array}{l} CO_2H\cdot CH_2\cdot CH{-}CMe\cdot CO_2H \\ \quad CO_2H\cdot CMe\cdot CH\cdot CH_2\cdot CO_2H \end{array}$$

(XXIV.)

The formation of these substances is, of course, part of the wider question, discussed in a recent paper by one of us (this vol., p. 951), relating to the ease of formation and the stability of *cyclo*butane derivatives. Further papers on this and allied subjects will shortly be presented to the Society; in the meantime, with regard to the example under consideration, it may merely be stated that the reaction leading to the ester, m. p. 87°, appears to be favoured by the use of a slight deficit of sodium ethoxide, and that in these circumstances its formation often occurs to such an extent as to suppress almost completely all products formed (compare the scheme outlined above) subsequently to the cyano-ester (XX).

All products of the condensation were carefully identified, the liquids, after analysis, being converted into crystalline derivatives, which were then directly compared with authentic specimens. Ethyl propionate and ethyl malonate were converted into propionamide and malonamide respectively. The cyanomethylglutaconic ester (XX) was hydrolysed to α-methylglutaconic acid, which proved to be identical with a specimen of this acid kindly lent by Prof. J. F. Thorpe. The methanetriacetic acid derivative (XIX), on hydrolysis, gave ω-methylmethanetriacetic acid (XXVII), which, as a degradation product of quinine (Skraup, *Monatsh.*, 1900, **21**, 879) and on account of its close relationship with *iso*camphoronic acid (XXVIII), is an acid of considerable interest. We have synthesised it for comparison with the acid obtained from the condensation product by a method which should leave no doubt as to its constitution: ethyl ω-cyanomethanetriacetate (XXV) (Ingold, *loc. cit.*) was converted into its sodio-derivative and then methylated; the methylated ester (XXVI),



$$CH\begin{cases} CH_2\cdot CO_2Et \\ CH(CN)\cdot CO_2Et \\ CH_2\cdot CO_2Et \end{cases} \longrightarrow CH\begin{cases} CH_2\cdot CO_2Et \\ CMe(CN)\cdot CO_2Et \\ CH_2\cdot CO_2Et \end{cases}$$

(XXV.) (XXVI.)

$$CH\begin{cases} CH_2\cdot CO_2H \\ CMe_2\cdot CO_2H \\ CH_2\cdot CO_2H \end{cases} \qquad CH\begin{cases} CH_2\cdot CO_2H \\ CHMe\cdot CO_2H \\ CH_2\cdot CO_2H \end{cases}$$

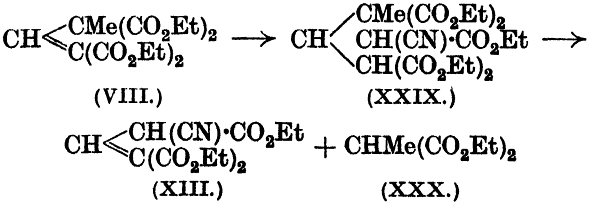
(XXVIII.) (XXVII.)

on hydrolysis by sulphuric acid, yielded ω-methylmethanetriacetic acid identical in all respects with the substance obtained from the products of the condensation described above.

From what has been said it might at first sight appear remarkable that the esters XXV and XXVI should be, as apparently they are, quite stable towards boiling alcoholic sodium ethoxide solution. If, however, their formulæ be compared with those of the methanetriacetic acid derivatives previously mentioned (IX, XVI, XVII, XIX, and XXI), it will be observed that each of the latter contains *at least two* branched acetic acid chains, and it would certainly seem, from the present investigation, to be a condition necessary for instability that at least two of the three acetic acid chains attached to the methane carbon atom should bear substituent groups.

That some such limit should exist is in full harmony with the spatial view of the matter, which, for reasons that cannot here be fully entered into, we have been led to adopt. There must be certain definite, necessary, *and sufficient* conditions, which cannot be traced or even adumbrated in a restricted investigation such as this. The question of definition requires experiments based on a wider plan, and some of these have now been commenced. By this means, it is hoped, the problem may be explored along some at least of its principal directions, but in the meantime it has seemed desirable to obtain some confirmation of a general character, at least so far as methanepolyacetic acid derivatives are concerned, by examining the ease of fission of a methanetriacetic ester containing as many substituents as could conveniently be introduced.

With this object in view the condensation of ethyl αγ-dicarboxy-α-methylglutaconate (VIII) with ethyl sodiocyanoacetate was investigated, and it was found, as anticipated, that the two substances reacted at the ordinary temperature with remarkable ease, yielding in the course of a few hours almost theoretical amounts of ethyl α-cyano-γ-carboxyglutaconate (XIII) and ethyl methylmalonate (XXX):



$$\mathrm{CH}{\lessgtr}\begin{matrix}\mathrm{CMe(CO_2Et)_2}\\ \mathrm{C(CO_2Et)_2}\end{matrix} \longrightarrow \mathrm{CH}\begin{matrix}\mathrm{CMe(CO_2Et)_2}\\ \mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{CH(CO_2Et)_2}\end{matrix} \longrightarrow$$

(VIII.) (XXIX.)

$$\mathrm{CH}{\lessgtr}\begin{matrix}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{C(CO_2Et)_2}\end{matrix} + \mathrm{CHMe(CO_2Et)_2}$$

(XIII.) (XXX.)

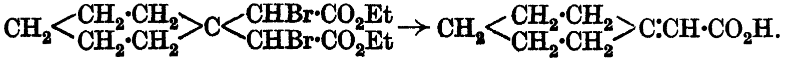
The former was identified by analysis and by conversion into the ester-imide (XV), and the latter by analysis and conversion into the amide. The intermediate methanetriacetic acid derivative

(XXIX) must have been very short-lived, for, in spite of the low temperature at which the condensation was carried out, no trace of it could be isolated.

When the nature of these condensations had been elucidated, the literature was searched for accounts of reactions having a similar character. The only example, however, which could be found of a reaction apparently involving a retrograde Michael condensation is the observation by Kötz and Zörnig (*J. pr. Chem.*, 1906, [ii], **74**, 427, *Anmerkung*) that ethyl benzylmalonate can be isolated from the product formed when ethyl sodiomalonate is allowed to react with ethyl αγ-dicarboxy-α-methylglutaconate. The mechanism of this reaction is doubtless analogous to that of the condensations described above, although Kötz and Zörnig do not appear to have examined their product as closely as is desirable for the purpose of establishing the matter definitely.

There are, however, on record a very large number of reactions in which the operation of the factors governing the phenomena discussed in the present paper is to be traced. Thus Kötz and Zörnig carried out many condensations between chloroform and the sodium compounds of various ketones, esters, and nitriles (for example, deoxybenzoin, ethyl methylmalonate, malononitrile) with the object of preparing compounds in which three organic residues had become attached to the methane carbon atom supplied by the chloroform. In no case, however, was a product of this constitution obtained, the sodium compound employed invariably reacting after the manner of ethyl sodiomalonate, if that were possible, or, in the case of compounds lacking the hydrogen atom necessary for this type of condensation, in such a way as to leave one of the halogen atoms of the chloroform molecule undisturbed. The reason for this is not difficult to discover; for in all the cases investigated the desired condensation products, had they been obtained, would have contained *three* branched acetic acid chains, a condition of the molecule incompatible with stability.

An illuminating instance of the elimination of a substituted acetic acid residue in a totally different type of reaction is that furnished by the conversion of ethyl αα′-dibromo*cyclo*hexane-1 : 1-diacetate to *cyclo*hexylideneacetic acid by hydrolysis (Beesley, Ingold, and Thorpe, T., 1915, **107**, 1080):



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CHBr\cdot CO_2Et}\\ \mathrm{CHBr\cdot CO_2Et}\end{matrix}\rightarrow \mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C{:}CH\cdot CO_2H}.$$

No reaction of a similar character has been observed with the corresponding derivative of ββ-dimethylglutaric acid, namely, the bromo-ester, $\mathrm{CMe_2(CHBr\cdot CO_2Et)_2}$, a fact which has been attributed (*loc. cit.*) to the *gem*-methyl groups together occupying less of the space surrounding the quaternary carbon atom than the C_5H_{10}**:** residue in the corresponding cyclic compound. The consideration of this and many similar instances, some of which occur in the literature of triphenylmethyl and its analogues, many in that which relates to the Michael and Knoevenagel condensations, leads, we consider inevitably, to the conclusion that, as suggested on p. 1585, spatial causes are at the root of all these phenomena, and amongst them the reactions described in this paper.

Reference to certain new derivatives of 6-ethoxy-2-pyrone, which were obtained incidentally in the course of the research, will be found at the end of the experimental portion.

EXPERIMENTAL.

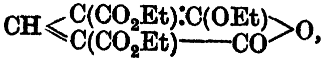
(A) *Preparation of α-Substituted Glutaconic Esters.*

Ethyl αγ-Dicarboxyglutaconate (VI).—The sodium compound of this ester was prepared by Conrad and Guthzeit's method (*Ber.*, 1882, **15**, 281), certain modifications, however, being introduced with the object of improving the yield. Coutelle, who made a detailed study of the reaction, states (*J. pr. Chem.*, 1906, [ii], **73**, 49) that the maximal yield is 41—42 per cent. of the theoretical, but by the following method it is possible to obtain 60 per cent. with certainty.

Ethyl malonate (160 grams) was added to a solution of sodium ethoxide prepared by dissolving 46 grams of sodium in 1 litre of absolute ethyl alcohol. When the temperature was between 30° and 35°, chloroform (60 grams) was poured in and the mixture allowed to remain until the violent ebullition caused by the heat developed in the reaction had subsided. The mixture was then heated for half an hour on a water-bath with a further quantity (20 grams) of chloroform and filtered while still hot. The yellow sodium compound (80 grams) separated from the filtrate on cooling and a further 25 grams were obtained by concentrating the mother-liquors to about one-sixth of their bulk.

The free ester was prepared from the sodium compound in the way recommended by Conrad and Guthzeit (*loc. cit.*).

Ethyl α-Carboxyglutaconate (*Ethyl* iso*Aconitate*, V).—For the preparation of ethyl *iso*aconitate ethyl dicarboxyglutaconate was first converted by heating at 200° into ethyl 6-ethoxy-2-pyrone-3 : 5-dicarboxylate,



$$CH\Big<\begin{matrix}C(CO_2Et){:}C(OEt)\\ C(CO_2Et)\text{——}CO\end{matrix}\Big>O,$$

which was then hydrolysed to the *iso*aconitate by means of cold 2·5 per cent. aqueous sodium hydroxide, as recommended by Guthzeit and Dessel (*Ber.*, 1889, **22**, 1413).

In working up large quantities it was found desirable to purify the pyrone carefully by crystallisation from ether, since when this was done it was unnecessary to distil the ethyl *iso*aconitate, an operation which was often troublesome unless carried out with small amounts of material.

Ethyl αγ-Dicarboxy-α-methylglutaconate (VIII).—This substance was prepared by methylating the yellow sodium compound of ethyl dicarboxyglutaconate in the manner described by Thole and Thorpe (T., 1911, **99**, 2197).

Ethyl α-carboxy-γ-methylglutaconate (VII) was obtained from ethyl dicarboxymethylglutaconate by the action of sodium ethoxide (Thole and Thorpe, *loc. cit.*).

(B) *Condensation of Ethyl α-Carboxyglutaconate (Ethyl* iso*Aconitate) with Ethyl Cyanoacetate. Isolation of Ethyl α-Cyanoglutaconate and Ethyl Malonate.*

Ethyl *iso*aconitate (26 grams; 1 mol.) was mixed with a suspension in absolute ethyl alcohol of ethyl sodiocyanoacetate prepared from 4·8 grams (slightly more than two atoms) of sodium, 75 c.c. of ethyl alcohol, and 22·6 grams (2 mols.) of ethyl cyanoacetate. The mixture, which at once became yellow owing to the formation of the sodium compound of ethyl *iso*aconitate, was allowed to remain for a short time at room temperature, and was then heated on the steam-bath for fifteen hours, at the end of which time most of the alcohol was distilled off and the residue mixed with water. The precipitated oil was extracted with ether, the acid substances remaining in the aqueous solution being recovered by acidifying and again extracting.

Ethyl Malonate (XI).

On distillation under diminished pressure, the neutral ester was found to consist chiefly of ethyl malonate, six grams of which were obtained in a pure condition, b. p. 104°/30 mm., by a second distillation. Its identity was proved by analysis (Found : C = 52·3; H = 7·3. Calc., C = 52·5; H = 7·5 per cent.), and by converting it into malonamide, which was compared with a known specimen and further identified by a mixed melting point determination.

The alcoholic distillate (above) was saturated with ammonia, and, two days later, mixed with concentrated aqueous ammonia.

The mixture was kept at room temperature for a further period of two days and then evaporated in a vacuum. The small residue proved to be almost pure malonamide, and, in spite of a careful search, no trace of acetamide could be detected (contrast section D).

The less volatile portion of the neutral fraction was very small in amount, but it yielded two crystalline substances, m. p. 116° and 179° respectively, which, however, were not obtained in quantities sufficient for further investigation.

Ethyl α-Cyanoglutaconate (X).

The acid extract, on evaporation, left a pale yellow, viscous oil, which could not be distilled; but which was found to consist essentially of ethyl cyanoglutaconate. The method of purification finally adopted was as follows. The oil was mixed with ether and shaken, first with water, and then for several hours with an aqueous suspension of precipitated calcium carbonate. The ester recovered by drying and evaporating the ethereal solution was converted, by mixing with an approximately equivalent quantity of ethyl-alcoholic sodium ethoxide, into its sodio-derivative, which was precipitated by adding ether, collected, and decomposed by means of cold dilute hydrochloric acid. The liberated ester, which consisted of pure ethyl cyanoglutaconate, was extracted by means of pure ether, the last traces of which were expelled in an evacuated desiccator (Found: $C = 56{\cdot}5$; $H = 6{\cdot}2$; $N = 7{\cdot}0$. Calc., $C = 56{\cdot}8$; $H = 6{\cdot}2$; $N = 6{\cdot}7$ per cent.).

The ester corresponded closely in its properties with the substance described by Guthzeit and Eyssen (*loc. cit.*). However, in order to identify it with certainty, it was converted by ethylation, by means of alcoholic sodium ethoxide and ethyl iodide, into ethyl α-cyano-α-ethylglutaconate (XII) (Found: $C = 60{\cdot}4$; $H = 7{\cdot}4$. Calc., $C = 60{\cdot}2$; $H = 7{\cdot}1$ per cent.), which had the melting point (79°) and "glass-wool-like" appearance mentioned by those authors.

(C) *Condensation of Ethyl αγ-Dicarboxyglutaconate with Ethyl Cyanoacetate: Isolation of Ethyl α-Cyano-γ-carboxyglutaconate, Ethyl αγ-Dicyanoglutaconate, and Ethyl Malonate.*

Ethyl cyanoacetate (22·6 grams; 2 mols.) was mixed with a solution of sodium ethoxide prepared by dissolving 4·6 grams of sodium (one atom) in 60 grams of absolute ethyl alcohol. When the precipitation of ethyl sodiocyanoacetate appeared to be complete, 36 grams (1 mol.) of the recrystallised and finely ground sodium compound of ethyl dicarboxyglutaconate (section A) were added and the mixture was heated with frequent shaking on a steam-bath for a period of eighteen hours, during which the sodium compound gradually dissolved and another much less strongly coloured substance separated from the brown solution. The product was poured into dilute hydrochloric acid and extracted with ether, the acidic substances being removed from the extract by washing with dilute aqueous sodium carbonate solution and recovered from the washings by acidifying and again extracting.

Ethyl Malonate (XI).

Most of the neutral ester boiled at 90–105°/10 mm., and this fraction on redistillation yielded pure ethyl malonate (Found: C = 52·4; H = 7·5. Calc., C = 52·5; H = 7·4 per cent.), which was satisfactorily identified by converting it into malonamide and comparing this with a genuine specimen.

A very small quantity of material boiling in the neighbourhood of 200°/10 mm. was also collected, and this, on keeping for a few days, partly solidified. The crystals were drained on porous porcelain, washed with ether, and recrystallised twice from this solvent. They separated in long needles, m. p. 93–94°, and must have consisted of ethyl 6-ethoxy-2-pyrone-3 : 5-dicarboxylate (Found: C = 54·7; H = 5·6. Calc., C = 54·9; H = 5·6 per cent.), although at the time none of this material was at hand for comparison. On keeping, the crystals partly liquefied, a property which the pyrone also possesses.

Ethyl α-Cyano-γ-carboxyglutaconate (XIII).

The acid extract (above), after being dried with sodium sulphate (calcium chloride caused the precipitation of a yellow calcium salt) and evaporated, left a yellow, viscous oil, which could not be distilled, but consisted chiefly of ethyl α-cyano-γ-carboxyglutaconate and a small quantity of ethyl αγ-dicyanoglutaconate, crystals of which could sometimes be obtained from it by keeping. The crude oil was triturated with cold dilute aqueous sodium hydroxide, which converted it into a biscuit-coloured mixture of sparingly soluble sodium compounds. These were collected, washed with hot water, and decomposed by cold dilute hydrochloric acid, the ester liberated being at once extracted with benzene, and the extract dried by shaking with sodium sulphate and evaporated at room temperature in a vacuum. The ethyl α-cyano-γ-carboxyglutaconate thus obtained was a pale yellow oil, giving with aqueous alcoholic ferric chloride a deep crimson colour (Found: C = 55·4; H = 6·2; N = 5·4. $C_{13}H_{17}O_6N$ requires C = 55·1; H = 6·0; N = 5·0 per cent.).

The ester appears to have been obtained previously by Errera (*Ber.*, 1898, **31**, 1243) by the action of ethyl cyanoacetate on ethyl ethoxymethylenemalonate, but no steps were taken to purify the product and no analysis is quoted.

In order to obtain a further check on the constitution of the substance, it was subjected to regulated hydrolysis by hydrochloric acid. It dissolved completely in the cold concentrated acid, but on warming an oil separated. This oil was, apparently, the acid ester (XIV), for on shaking for a few minutes with the hot concentrated acid it was quickly converted into a sparingly soluble, crystalline substance, which melted at 199° and had all the characteristics of ethyl 6-hydroxy-2-keto-$\Delta^{3:5}$-dihydropyridine (XV) (a modification of ethyl 2 : 6-dihydroxynicotinate, and of the imide-ester of dicarboxyglutaconic acid. Compare Guthzeit, *Ber.*, 1893, **26**, 2796; Errera, *loc. cit.*, and Guthzeit and Eyssen, *loc. cit.*).

The *sodio*-compound, obtained in the course of the above separation, and prepared from the pure cyano-ester by treatment with sodium hydroxide, was a pale yellow, crystalline substance sparingly soluble in water and alcohol (Found: Na = 7·2. $C_{13}H_{16}O_6NNa$ requires Na = 7·5 per cent.).

The *calcio*-derivative, a yellow, crystalline powder, was prepared from the cyano-ester, aqueous calcium chloride, and ammonium hydroxide (Found: Ca = 6·3. $C_{26}H_{32}O_{12}N_2Ca$ requires Ca = 6·6 per cent.).

Ethyl $\alpha\gamma$-*Dicyanoglutaconate* (XVIII).

The washings from the foregoing sodium compounds, on keeping, deposited an almost colourless sodium compound, which, on trituration with dilute hydrochloric acid, yielded a bright yellow, crystalline substance. This was identified as ethyl dicyanoglutaconate (Errera, *Gazzetta*, 1898, [ii], **27**, 393; Ruhemann and Browning, *loc. cit.*) by its melting point, 184—186°, nitrogen content (Found: N = 11·6. Calc., N = 11·8 per cent.), and by direct comparison with an authentic specimen.

Formation of Ethyl $\alpha\gamma$-*Dicyanoglutaconate from Ethyl* α-*Cyano*-γ-*carboxyglutaconate and Ethyl Cyanoacetate.*

Ethyl cyanoacetate (2·3 grams) and ethyl sodio-α-cyano-γ-carboxyglutaconate (3 grams) were successively added to a solution of sodium ethoxide prepared from 0·23 gram of sodium and 6 grams of absolute ethyl alcohol. The mixture was heated on a water-bath for twenty-four hours and then evaporated, the residue being treated with dilute hydrochloric acid and the precipitated oil divided into neutral and acid fractions by ether and sodium carbonate in the usual way. The neutral fraction appeared to consist of ethyl malonate, but the quantity was very small, and it was therefore not identified with certainty. The acid fraction was separated into its constituents by converting it into sodium compounds and extracting these with hot water as described on p. 1594, and in this way a small amount of ethyl αγ-dicyanoglutaconate, as well as a considerable quantity of unchanged ethyl α-cyano-γ-carboxyglutaconate, were isolated in the pure condition.

(D) *Condensation of Ethyl α-Carboxy-γ-methylglutaconate with Ethyl Cyanoacetate: Isolation of ω-Methylmethanetriacetic Acid, Ethyl α-Cyano-γ-methylglutaconate, Ethyl αγ-Dicyanoglutaconate, Ethyl Malonate, and Ethyl Propionate.*

In carrying out this condensation it was found necessary to use a slight excess of sodium ethoxide in order to avoid the formation of the *cyclo*butane derivative (XXIII).

Ethyl cyanoacetate (22·6 grams; 2 mols.) and ethyl α-carboxy-γ-methylglutaconate (27·2 grams; 1 mol.) (section A) were added in succession to a solution of sodium ethoxide prepared by dissolving sodium (5 grams; 2·1 atoms) in absolute ethyl alcohol (70 c.c.). The mixture was heated for thirty hours and then distilled until the temperature reached 100°.

Ethyl Propionate (XXII).

The distillate contained a quantity of ethyl propionate, which, however, could not be separated from the large excess of ethyl alcohol accompanying it. It was therefore converted into the amide by saturating the alcoholic solution with ammonia and, after some hours, adding concentrated aqueous ammonia. The amide thus obtained was recrystallised from a small amount of water and identified as propionamide by analysis (Found: C = 49·3; H = 9·7; N = 19·4. Calc., C = 49·3; H = 9·6; N = 19·2 per cent.), by its m. p. (79°) and characteristic appearance, and by direct comparison with a specimen prepared from an authentic sample of ethyl propionate.

Ethyl Malonate (XI).

The pasty residue from the distillation (p. 1596) was mixed with water and extracted with ether. The oil thus obtained boiled almost entirely between 90° and 100°/15 mm., and on redistillation at atmospheric pressure yielded 10 grams of pure ethyl malonate (Found: C = 52·4; H = 7·5. Calc., C = 52·5; H = 7·5 per cent.), which was identified, as before, by conversion into malonamide.

A further quantity was obtained by esterifying, by means of ethyl alcohol and sulphuric acid, the acid substances recovered from the alkaline solution from which the sodio-derivative of ethyl dicyanoglutaconate had crystallised (below), the neutral esterification product consisting of about equal parts of ethyl malonate and ethyl α-carboxy-γ-methylglutaconate, which were easily separated by distillation.

Ethyl α-Cyano-γ-methylglutaconate (XX).

The alkaline solution from which the ethyl malonate was extracted was acidified and again extracted with ether, the products being separated into acid and quasi-acid fractions by washing with 10 per cent. aqueous sodium carbonate solution. The quasi-acid fraction boiled at 160—170°/15 mm., and consisted almost entirely of *ethyl α-cyano-γ-methylglutaconate*, 14 grams of which were obtained on redistillation as a colourless oil, b. p. 160°/15 mm. (Found: C = 58·3; H = 6·9; N = 6·5. $C_{11}H_{15}O_4N$ requires C = 58·6; H = 6·7; N = 6·2 per cent.). It gave a deep reddish-brown colour with aqueous-alcoholic ferric chloride.

As mentioned above, a further quantity of the substance was obtained by esterifying the acid products.

In order to confirm its constitution, the ester was hydrolysed by boiling with 50 per cent. sulphuric acid. The product, extracted by ether and crystallised from water, was identified as α-methylglutaconic acid by analysis (Found: C = 50·1; H = 5·7. Calc., C = 50·0; H = 5·5 per cent.), by direct comparison with a genuine specimen, and by a mixed melting-point determination.

Ethyl αγ-Dicyanoglutaconate (XVIII).

The sodium carbonate washings (above) quickly deposited a very pale brown, crystalline sodium compound, which, after purification by recrystallisation from water or alcohol, melted at 263—265° and evidently consisted of ethyl sodiodicyanoglutaconate (Found: Na = 8·9. Calc., Na = 8·9 per cent.).

The free dicyano-ester, prepared from the sodium compound, was identified by comparison with a known specimen and by analysis (Found: C = 54·5; H = 5·4; N = 11·7. Calc., C = 55·9; H = 5·1; N = 11·9 per cent.), the results of which, although not agreeing very closely with the theoretical values, are similar to the figures obtained by Errera (*loc. cit.*) and by Ruhemann and Browning (*loc. cit.*), and are to be attributed to the well-known tendency of the substance to retain small amounts of water with great persistency.

Formation of Ethyl αγ-Dicyanoglutaconate from Ethyl α-Cyano-γ-methylglutaconate and Ethyl Cyanoacetate.

Ethyl α-cyano-γ-methylglutaconate was heated with an alcoholic solution containing two molecular proportions of ethyl sodiocyanoacetate. Although an excess of sodium ethoxide was present, a considerable amount of conversion into the *cyclo*butane derivative (XXIII) occurred. However, on dividing the product into neutral, quasi-acid, and acid portions in the manner previously described, this became separated from the dicyano-ester, which was isolated and identified as in the preceding instance.

Formation of Derivatives of ω-Methylmethanetriacetic Acid.

In order to isolate derivatives of ω-methylmethanetriacetic acid from the product of condensation of α-cyano-γ-methylglutaconic acid with ethyl sodiocyanoacetate, it was necessary to carry out the condensation entirely at room temperature. The reaction mixture, prepared as described on p. 1596, was therefore allowed to remain with occasional shaking for twenty-four hours at the ordinary temperature, and was then mixed with water and separated by means of ether and aqueous sodium carbonate into neutral, quasi-acid, and acid portions.

The neutral fraction on distillation yielded ethyl malonate and a small amount of a viscous liquid boiling in the neighbourhood of 200°/10 mm.

The quasi-acid fraction consisted almost entirely of ethyl α-cyano-γ-methylglutaconate, although a small amount of a similar fraction of high b. p. was separated from it.

The acid fraction contained no trace of ethyl αγ-dicyanoglutaconate (compare section E), but when esterified and distilled gave the substance of high b. p. along with ethyl malonate and an intermediate fraction of indefinite boiling point.

The less volatile substance obtained in all these ways consisted apparently of *ethyl ω-cyano-ω′-carboxy-ω″-methylmethanetriacetate* (XIX), for on hydrolysis by 50 per cent. sulphuric acid (compare p. 1600) it yielded *ω-methylmethanetriacetic acid* (Found : C = 46·6; H = 6·0. $C_8H_{12}O_6$ requires C = 47·0; H = 5·9 per cent.), which, after crystallisation from ethyl acetate, melted at 136—137° and was identical in all respects with the acid synthesised (section F) for comparison.

(E) *Condensation of Ethyl αγ-Dicarboxy-α-methylglutaconate with Ethyl Cyanoacetate : Isolation of Ethyl Methylmalonate and Ethyl α-Cyano-γ-carboxyglutaconate.*

Ethyl αγ-dicyano-α-methylglutaconate (1 mol.) (section A) was condensed with ethyl sodiocyanoacetate (2 mols.) as in the preceding instances, excepting that, as in this case the reaction proceeded with extraordinary ease, the mixture was kept at room temperature for two hours only, and was then worked up for the products, which were separated into neutral and acid portions by means of ether and sodium carbonate.

Ethyl Methylmalonate (XXX).

Almost the whole of the neutral product distilled in the neighbourhood of 100°/10 mm., and on redistillation at atmospheric pressure boiled constantly at 195°. That this consisted of pure ethyl methylmalonate was proved by analysis (Found : C = 55·2; H = 8·0. Calc., C = 55·2; H = 8·0 per cent.), and by conversion into methylmalonamide, which was obtained in good yield and identified with an authentic specimen.

The amide contained no admixed malonamide, and, therefore, the reaction product could have contained no ethyl malonate (see below).

Ethyl α-Cyano-γ-carboxyglutaconate (XIII).

This substance (Found : C = 55·6; H = 6·3. Calc., C = 55·1; H = 6·0 per cent.) was isolated from the acid product of the condensation in the manner described in connexion with the previous reaction (section C) in which it was obtained, and was identified by means of its characteristic sodium derivative (Found : Na = 7·3. Calc., Na = 7·5 per cent.) and by conversion into the imide (XV) by boiling with hydrochloric acid.

No ethyl αγ-dicyanoglutaconate was isolated from this condensation (compare that described on p. 1596), and it would appear that the formation of this substance by the action of ethyl sodiocyanoacetate on compounds such as ethyl α-cyano-γ-methylglutaconate and ethyl α-cyano-γ-carboxyglutaconate requires a higher temperature than that of the room.

(F) *Preparation of ω-Methylmethanetriacetic Acid from Ethyl ω-Cyanomethanetriacetate.*

These experiments were carried out in order to obtain a specimen of ω-methylmethanetriacetic acid for comparison with the acid obtained in the condensation described in section D. The starting material, ethyl ω-cyanomethanetriacetate, was prepared by the method described in a recent communication (Ingold, this vol., p. 352).

Ethyl ω-Cyano-ω-methylmethanetriacetate (XXVI).

Ethyl ω-cyanomethanetriacetate was mixed with an alcoholic solution containing one equivalent of sodium ethoxide, and then with a slight excess of methyl iodide. The solution was boiled until neutral to moistened litmus, and the esters were isolated by adding water and extracting with ether. *Ethyl ω-cyano-ω-methylmethanetriacetate* was obtained, by distillation under diminished pressure, as a colourless, viscous oil, b. p. 206—208°/12 mm. (Found: C = 57·6; H = 7·5. $C_{15}H_{23}O_6N$ requires C = 57·5; H = 7·3 per cent.).

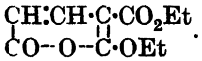
ω-Methylmethanetriacetic Acid (XXVII).

A mixture of the pure methylated cyano-ester and an equal volume of cold concentrated sulphuric acid was diluted, after twelve hours' keeping, with sufficient water to cause a slight precipitation of oil, and then heated for seven hours on a sand-bath, a further quantity of water being added and the reflux condenser removed towards the end of this period after the evolution of carbon dioxide had ceased. The solution was cooled, saturated with ammonium sulphate, and extracted repeatedly with ether. The colourless syrup which remained on drying and evaporating the ether immediately solidified with evolution of heat on touching with a glass rod. The acid was crystallised from ethyl acetate for analysis; it separated in small, dense prisms, m. p. 137—138° [Found: C = 46·9; H = 6·0. M (by titration) = 203·1. Calc., C = 47·0; H = 5·9 per cent.; M = 204].

(G) *Note on some Derivatives of 6-Ethoxy-2-pyrone.*

The following compounds were obtained incidentally during the preparation of some of the materials required for this research. They have not been investigated in detail, but their constitutions appear to follow from their modes of formation, and it has been thought desirable to append a brief description.

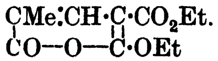
Ethyl 6-Ethoxy-2-pyrone-5-carboxylate,



$$\begin{matrix}CH{:}CH{\cdot}C{\cdot}CO_2Et\\ CO{-}O{-}C{\cdot}OEt\end{matrix}.$$

Ethyl *iso*aconitate is apt to decompose on distillation and on one occasion the pyrone was isolated from the dark residue obtained in this manner. It was purified by rubbing with ether and crystallisation from ethyl acetate, from which it separated in needles, m. p. 132° (Found: C = 56·7; H = 5·3. $C_{10}H_{12}O_5$ requires C = 56·6; H = 5·6 per cent.). With aqueous alcoholic ferric chloride it formed a deep crimson coloration.

Ethyl 6-Ethoxy-3-methyl-2-pyrone-5-carboxylate,



$$\begin{matrix}CMe{:}CH{\cdot}C{\cdot}CO_2Et.\\ CO{-}O{-}C{\cdot}OEt\end{matrix}$$

This compound was invariably formed to some extent when large quantities of ethyl α-carboxy-γ-methylglutaconate were distilled at a time, and occasionally it crystallised from the distillate. The material obtained in this way was purified for analysis by crystallisation from ethyl acetate. It separated in colourless, transparent strips or blades, usually long and very thin, a typical size being 20 mm. × 1 mm. × 0·05 mm. (Found: C = 58·1; H = 6·1. $C_{11}H_{14}O_5$ requires C = 58·3; H = 6·4 per cent. M, by the cryoscopic method in benzene, = 224. Calc., M = 226). It melted at 94° and gave no distinct coloration with ferric chloride.

We desire to express our gratitude to Professor J. F. Thorpe for his interest in these experiments and for much very valuable advice; also to the Chemical Society for a grant from their Research Fund which has greatly facilitated the work.

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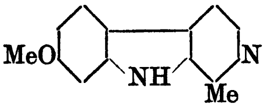
[*Received, August* 13*th*, 1921.]

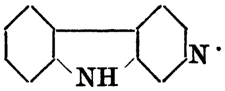
CLXXXV.—*Harmine and Harmaline. Part V. The Synthesis of Norharman.*

By William Ogilvy Kermack, William Henry Perkin, jun., and Robert Robinson.

In Parts III and IV of this research (T., 1919, **115**, 933 *et seq.*) evidence was brought forward and discussed which seemed to leave little doubt that harmine has the constitution I, whilst two possibilities remain for harmaline (dihydroharmine), the decision between which can only be made after the accumulation of further data.



(I.)

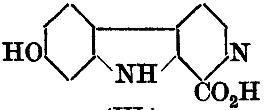


(II.)

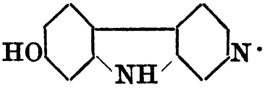
It appeared desirable, however, to support the strong analytical arguments by synthesis, and especially so in view of the fact that the fused pyridine–pyrrole nucleus type represents a domain of organic chemistry which has hitherto remained almost unexplored. In planning the synthetic investigation we have had always in view the systematic study of the methods available for the preparation of the more characteristic members of this group of bases, and accordingly in the first instance chose to attack the problem of the synthesis of 4-carboline (II), which can be regarded as the true parent substance of harmine and harmaline.

Harmine is methylmethoxy-4-carboline, and since the compounds obtained by elimination of the methyl and methoxy-groups from harmine are respectively termed norharmine and harman, it is clear that 4-carboline may also be called norharman in order to emphasise its relation with the harmala group of alkaloids.

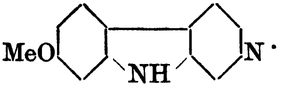
Two methods have now been devised for the degradation of harmine to norharman, and the first of these arose from the investigation of harmolic acid, which O. Fischer (*Ber.*, 1889, **22**, 642) produced by the alkali fusion of harmol, the phenol obtained by the demethylation of harmine. An erroneous composition was assigned by Fischer to this substance, which appears to be a molecular compound of norharmolcarboxylic acid (III) with its normal sulphate, and from which the sulphuric acid is readily removed by solution in dilute ammonia and precipitation with acetic acid. The fusion of harmol with potassium hydroxide, therefore, merely oxidises the methyl group to carboxyl. On heating norharmolcarboxylic acid with glycerol, the carboxyl group is eliminated and norharmol (IV) is obtained.



(III.)



(IV.)

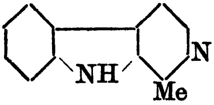


(V.)

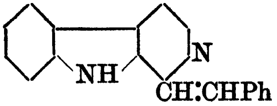
This phenolic base is certainly identical with that which was obtained by O. Fischer (*loc. cit.*) by heating harmolic acid, although the specimen was apparently not analytically pure. The nature of norharmol is clearly proved by the fact that on methylation it yields norharmine (V). On distillation with zinc dust in a stream of hydrogen, norharmol is converted into norharman (II).

The second process consists in applying to harman the method whereby harmine was degraded to norharmine (Perkin and Robinson, T., 1912, **101**, 1778).

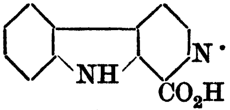
Unfortunately, the paucity of material at our disposal did not permit of an examination of the intermediate stages in the degradation of harman to norharman, but at all stages the substances closely resembled the analogous compounds derived from harmine. Harman (VI) was converted by boiling with benzaldehyde into benzylideneharman (VII), isolated as a sparingly soluble hydrochloride, and this was oxidised by potassium permanganate in pyridine solution with formation of norharmancarboxylic acid (VIII), which yielded norharman (II) on heating with glycerol. Norharman is a beautifully crystalline compound melting at 198° and very similar to harman in its properties.



(VI.)



(VII.)

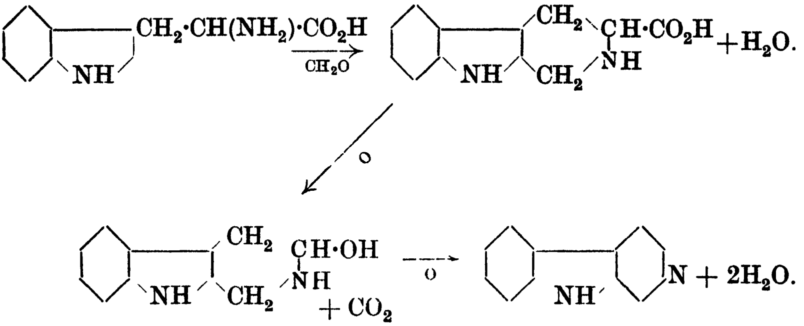


(VIII.)

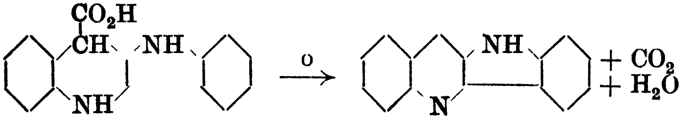
The interest attaching to harman, which was first obtained by O. Fischer (*Chem. Zentr.*, 1901, i, 958) from harmine by the stages harmol and aminoharman, is much increased by the observation of Späth (*Monatsh.*, 1919, **40**, 351) that it is identical with the alkaloid aribine from *Araribra rubra Mart.* and also with loturine from *Symplocosa racemosa* (*Monatsh.*, 1920, **41**, 297), whilst colloturine is possibly a crystalline modification. It should also be noted that

Späth confirms the fact, stated in Part IV of this research, that the true melting point of harman is 238°, although it is very easy to obtain a lower value.

The relation between harman and tryptophan was discussed in Parts III and IV of this inquiry, and becomes much more significant in view of the fact mentioned above that harman occurs in nature. Our further observations in this connexion will be found in the experimental portion on p. 1616, and it will suffice to point out that harman may be obtained by condensing tryptophan with acetaldehyde in dilute sulphuric acid solution and subsequently oxidising the product with chromic acid. Obviously the replacement of acetaldehyde by formaldehyde in this process should lead to the formation of norharman, and this proved to be the case, and the product was identical with that which had been obtained by the degradation of harmine. The mechanism of these reactions we conceive to be the following, illustrated in the case of the formation of norharman.

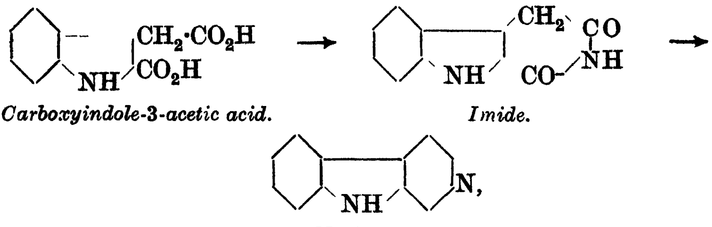


A very similar reaction, in which an oxidation is accompanied by the elimination of a carboxyl group, is to be found in the conversion of dihydroflavindine (IX) into quindoline (X), a change which can be effected with extraordinary facility, and even by shaking an alkaline solution with air at the room temperature (Fichter and Rohner, *Ber.*, 1910, **43**, 3489).



(IX.) (X.)

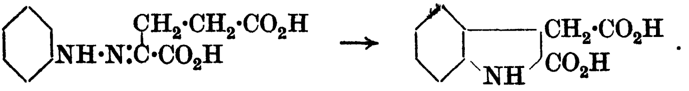
The production of norharman from tryptophan depends on a reaction of a somewhat special type, and as we desired to elaborate more generally applicable methods, attempts were made to build up the ring system from simple indole derivatives. Our first idea was to attempt the synthesis of norharman by the following stages,

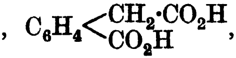
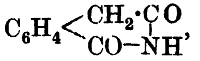


2-*Carboxyindole*-3-*acetic acid.* *Imide.*

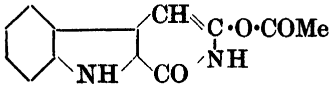
Norharman.

and we accordingly prepared considerable quantities of the 2-carboxyindole-3-acetic acid from α-ketoglutaric acid and phenylhydrazine by the process of Wislicenus and Waldmüller (*Ber.*, 1911, **44**, 1572):

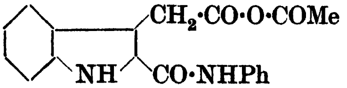


Several well-characterised derivatives of the acid were prepared, such as the dimethyl ester (m. p. 127°), the anhydride (m. p. 250°), and the acid amide (m. p. 244°), but all attempts to obtain the imide either (i) by the action of heat on the amide, (ii) by passing ammonia over the heated anhydride, or (iii) by the action of alcoholic ammonia on the dimethyl ester at elevated temperatures and pressures were unsuccessful. This is remarkable when it is remembered how readily homophthalic acid,  $C_6H_4{<}\begin{smallmatrix}CH_2{\cdot}CO_2H\\ CO_2H\end{smallmatrix}$, is converted into homophthalimide,  $C_6H_4{<}\begin{smallmatrix}CH_2{\cdot}CO\\ CO{-}NH\end{smallmatrix}$, by the action of heat on its ammonium salt.

It is true that the amide of 2-carboxyindole-3-acetic acid on treatment with a mixture of acetic anhydride and acetyl chloride yields a substance, $C_{13}H_{10}O_3N_3$, which appears to be the acetyl derivative of the enimic modification of the imide (XI), but we have not been successful up to the present in attempts to remove the acetyl group and obtain the imide itself. On the other hand, the anilide of 2-carboxyindole-3-acetic acid yields a mixed anhydride with acetic acid (XII) when treated in a similar way.

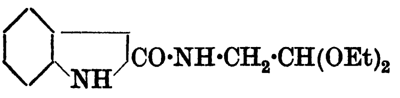


(XI.)

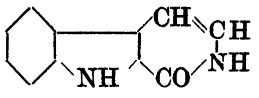


(XII.)

The next series of experiments was based on the hypothesis that indole-2-carboxyacetalylamide (XIII) might be induced to undergo internal condensation with the formation of the *iso*carbostyril of the norharman series (XIV), from which norharman could probably be obtained by some process of vigorous reduction.



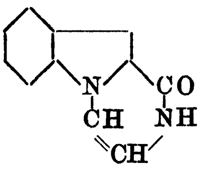
(XIII.)



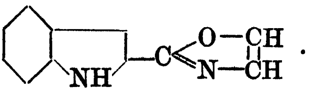
(XIV.)

In connexion with this series of experiments, we first worked out a generally applicable method for the preparation of the chlorides of indole-2-carboxylic acid and allied acids, which consists in allowing the acid to react with phosphorus pentachloride in the presence of acetyl chloride and at the end of the reaction removing the excess of acetyl chloride and phosphoryl chloride by distillation in a high vacuum. The residual chloride is usually sufficiently pure to be directly employed in the preparation of derivatives and the process is convenient.

The chloride of indole-3-carboxylic acid reacts readily with aminoacetal (acetalylamine), and indole-2-carboxyacetalylamide (XIII) is a crystalline substance, melting at 133°, which may be converted by the action of a saturated solution of hydrogen chloride in alcohol at 40—45° into a sparingly soluble, pale yellow, crystalline substance melting at 247°. This compound has the composition $C_{11}H_8ON_2$, and is thus derived from the acetalylamide by loss of two molecules of alcohol. It was natural therefore to assume that it was the expected ketodihydronorharman (XIV), but this view was soon found to be untenable, since all attempts to convert the substance into norharman were unsuccessful and a careful study of the reactions of the compound, described in detail on p. 1627, indicated the existence of a free position in the pyrrole nucleus. There appear to be only two other directions in which indole-2-carboxyacetalylamide may lose two molecules of alcohol, and these lead to the expressions XV and XVI for the substance melting at 247°.

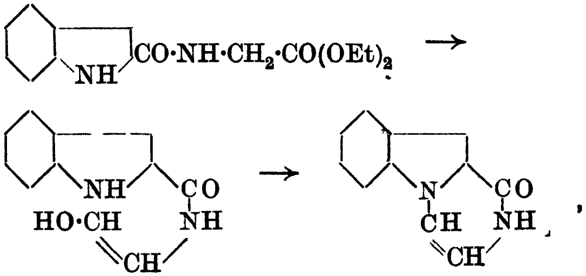


(XV.)

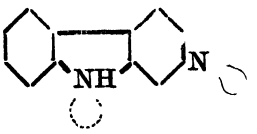


(XVI.)

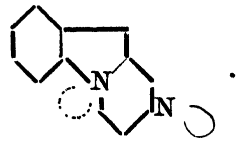
However, the compound appears to possess a —CO—NH— group capable of enimisation, and its phenolic properties are not in harmony with the oxazole possibility (XVI), against which may also be urged the melting point and crystalline character of the substance and, much more conclusive, the fact (*vid. infra*) that 1 : 3-dimethylindole-2-carboxyacetalylamide does not undergo an internal condensation analogous to those described in this communication, although the oxazole possibility remains open. It is clear, therefore, that the formation of the ring during the action of alcoholic hydrogen chloride on indole-2-carboxyacetalylamide has taken place with the help of the hydrogen atom of the —NH— group in the indole nucleus according to the scheme



and the substance thus produced has been called 5-keto-4 : 5-dihydroindolediazine (1 : 4) in accordance with a system of nomenclature detailed on p. 1642. Substances of this type do not appear to have been previously prepared, but it is evident that they are readily formed and are very stable. Up to the present oxygenated carbostyril-like derivatives only have been obtained, but there is no reason why the indolediazines themselves should be incapable of existence and these bases would probably be found to be of completely aromatic type. That this is possible is seen by a comparison of the cyclic conjugated formulæ which can be assigned to 4-carboline (XVII) and indolediazine (1 : 4) (XVIII) (compare Perkin and Robinson, T., 1919, **115**, 943).

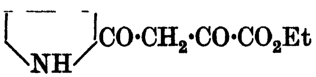


(XVII.)

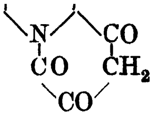


(XVIII.)

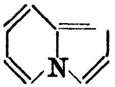
It is proposed to make attempts to produce substances of this type, which clearly have an interest in connexion with the theory of polynuclear aromatic compounds. Quite analogous substances of a similar nature, but containing the pyrrole nitrogen atom only, have already been obtained. Angeli (*Ber.*, 1890, **23**, 1793) found that ethyl pyrroylpyruvate (XIX) underwent ring-closure on treatment with alkaline carbonates with formation of the imine-anhydride of pyrroylpyruvic acid (XX).



(XIX.)



(XX.)

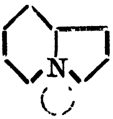


(XXI.)

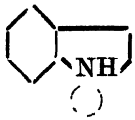
The parent substance, an isomeride of indole, was designated pyrindole by Angeli, and this extremely interesting compound has actually been obtained by Scholtz (*Ber.*, 1912, **45**, 734). α-Picoline is converted by acetic anhydride at 200—220° into a compound, $C_{12}H_{11}O_2N$, called picolide and the reaction occurs according to the equation:

$$C_6H_7N + 2(CH_3\cdot CO)_2O = C_{12}H_{11}O_2N + CH_3\cdot CO_2H + 2H_2O.$$

Picolide yields a feeble base, C_8H_7N, when it is boiled with hydrochloric acid, and this substance was the subject of further investigations (Scholtz, *Ber.*, 1912, **45**, 1718; Scholtz and Fraude, *Ber.*, 1913, **46**, 1069), which resulted in the demonstration that it has the constitution XXI. The feeble basicity of this compound and its resemblance in chemical character to pyrrole and indole are well represented in the cyclic conjugated formulæ XXII and XXIII for pyrrocoline (pyrindole) * and indole respectively.



(XXII.)



(XXIII.)

The elucidation of the nature of the substance of melting point 247° renders it very probable that Ciamician and Zatti's anhydride of indole-2-carboxylic acid, obtained by the action of acetic anhydride on the acid (*Ber.*, 1888, **21**, 1932), has the constitution XXIV. This yellow, crystalline substance melts at 312—315°, and whilst unaffected by aqueous alkalis is hydrolysed by alcoholic potassium hydroxide with formation of potassium indole-2-carboxylate.

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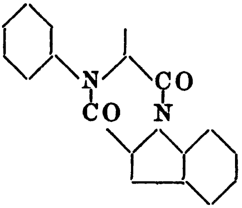
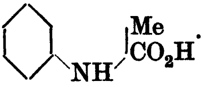
* The substance C_8H_7N was at first called "pyrrocoline" and later "pyrindole," in accordance with Angeli's suggestion. The name pyrindole should, however, be reserved for substances containing fused pyridine and pyrrole nuclei (T., 1912, **101**, 1787), and it would avoid the possibility of confusion if Scholtz's compound could retain its original name. The alternative device of renaming the fused pyridine–pyrrole nucleus "pyrindoline" would, unfortunately, lead to the expression "quinindoline" for a fused quinoline–pyrrole nucleus, and this name has already been employed to denote a tetranuclear base obtained by Gabriel and Eschenbach (*Ber.*, 1897, **30**, 3020).



(XXIV.)

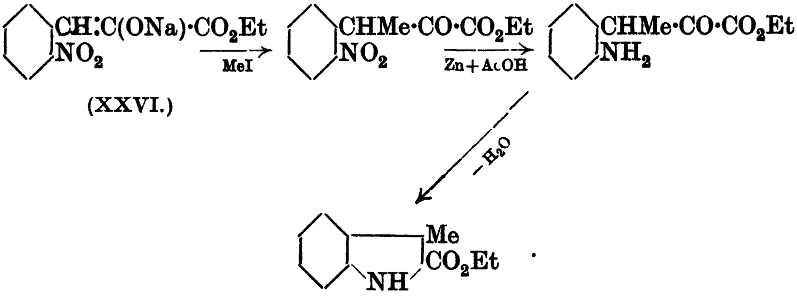


(XXV.)

The further study of the internal condensations of acetalylamides derived from substituted indole-2-carboxylic acids has given results which afford important support to our views on the constitution of the substance melting at 247°, and in the first place the behaviour of the acetalylamide of 3-methylindole-2-carboxylic acid (scatole-carboxylic acid) (XXV) was investigated.

This acid, which was at one time confused with indoleacetic acid, obtained by H. and E. Salkowski (*Ber.*, 1880, **13**, 191, 2217) from the products of the putrefaction of the proteins in animal matter, was synthesised by Arnold (*Annalen*, 1888, **246**, 334) from the phenylhydrazone of α-ketobutyric acid, $CH_3\cdot CH_2\cdot C(N_2H\cdot C_6H_5)\cdot CO_2H$, by the action of alcoholic sulphuric acid and by Ciamician and Magnanini (*Ber.*, 1888, **21**, 1927) from scatole, sodium, and carbon dioxide. We have found a new method for synthesising the acid which gives good results, and is as follows:

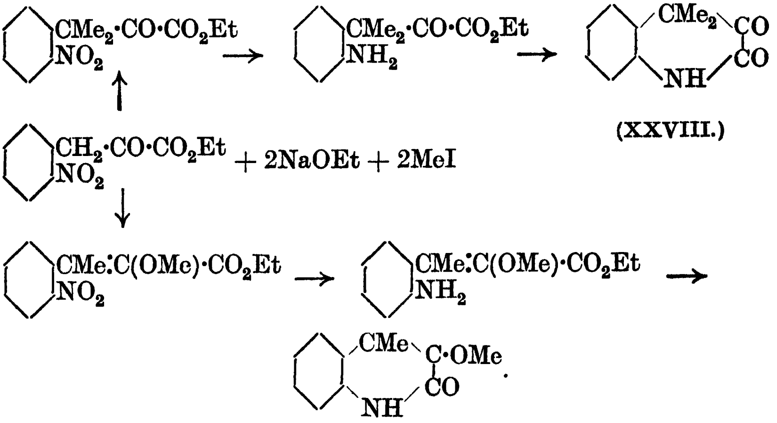
o-Nitrotoluene and ethyl oxalate are condensed by means of alcoholic sodium ethoxide in the manner described by Reissert (*Ber.*, 1897, **30**, 1030) to the sodium derivative of ethyl *o*-nitrophenylpyruvate (XXVI), which is then directly treated with methyl iodide, and the product on reduction with zinc dust and acetic acid yields ethyl 3-methylindole-2-carboxylate (XXVII), from which the acid is readily obtained by hydrolysis. The process is illustrated in the scheme given below:



(XXVI.)

(XXVII.)

In the course of the series of reactions just described there is also formed in relatively small amount a substance, $C_{11}H_{11}O_2N$ (m. p. 217°), which is not an ester and therefore probably owes its existence to the introduction of two methyl groups during the treatment of the sodium derivative of ethyl *o*-nitrophenylpyruvate with methyl iodide. There are two possibilities leading to the formulæ XXVIII and XXIX for this by-product.

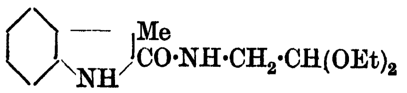


(XXVIII.)

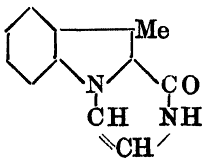
(XXIX.)

A Zeisel determination proved that the substance, $C_{11}H_{11}O_2N$, contains a methoxyl group, and it is therefore clear that the second alternative must be accepted and that the substance is 3-methoxy-4-methyl-α-quinolone.

When the chloride of 3-methylindole-2-carboxylic acid is treated with aminoacetal, combination occurs with facility and 3-methylindole-2-carboxyacetalylamide (m. p. 115°) (XXX) is produced. This substance, on treatment with alcoholic hydrogen chloride, yields a compound, $C_{12}H_{10}ON_2$, which melts at 242° and closely resembles the substance of melting point 247° obtained in a similar manner from indole-2-carboxyacetalylamide. In this example it will be noted that ring formation can only occur in the direction already postulated in the case of the substance melting at 247°, and the new compound (m. p. 242°) must be 5-keto-7-methyl-4 : 5-dihydroindolediazine (1 : 4) (XXXI).

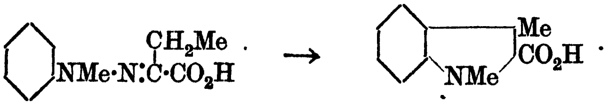


(XXX.)

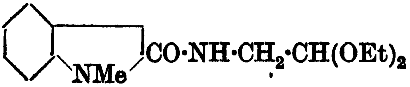


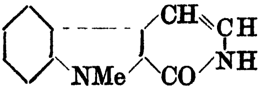
(XXXI.)

In order to examine the behaviour of a 1 : 3-disubstituted indole-2-carboxyacetalylamide, we instituted a series of experiments in which the starting point was 1 : 3-dimethylindole-2-carboxylic acid (XXXII), readily prepared in the following interesting manner. α-Ketobutyric acid, $CH_3 \cdot CH_2 \cdot CO \cdot CO_2H$ (Wislicenus and Arnold, *Annalen*, 1888, **246**, 333), reacts very readily with phenylmethylhydrazine, $C_6H_5 \cdot NMe \cdot NH_2$, and it is remarkable that the hydrazone is converted, merely by heating on the steam-bath with dilute hydrochloric acid, almost quantitatively into 1 : 3-dimethylindole-2-carboxylic acid (m. p. 213°) :

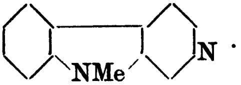

(XXXII.)

The chloride of this acid also combines with aminoacetal, yielding a crystalline substance, $C_{10}H_{10}N \cdot CO \cdot NH \cdot CH_2 \cdot CH(OEt)_2$, which melts at 111° and resembles in many ways the other similarly constituted acetalylamides described in this communication. It does not undergo ring formation when treated with alcoholic hydrogen chloride, a behaviour which was to be expected because the two positions essential to ring formation are occupied by methyl groups. The observation is, however, of much interest, as it disposes of the possibility that the substances which we have regarded as indolediazine derivatives are indyloxazoles (*vid. supra*). From the foregoing it became obvious that the particular synthetic method which depends on ring-closure of an indole-2-carboxyacetalylamide could lead to a derivative of norharman only if the 1-position in the indole nucleus is occupied by a substituent, and we accordingly applied the process to 1-methylindole-2-carboxylic acid, which was prepared by the method of E. Fischer and Hess (*Ber.*, 1884, **17**, 561). The chloride of this acid was converted into 1-methylindole-2-carboxyacetalylamide (m. p. 107°) (XXXIII) in the usual manner, and this substance was fortunately readily converted by alcoholic hydrochloric acid into 2-keto-1-methyl-2 : 3-dihydro-4-carboline (m. p. 242°) (XXXIV). This is a colourless substance, very different in its properties from the indolediazine derivatives, and resembling norharman more especially in the blue fluorescence which it exhibits in acid solution.


(XXXIII.)


(XXXIV.)

On distillation with zinc dust in a stream of hydrogen, norharman, possibly mixed with its methyl derivative (XXXV), was obtained. The purification of the crude product is described on p. 1638 and was tedious and difficult, but ultimately a pure specimen was obtained and proved to be identical in all respects with norharman obtained as detailed above from harmine and tryptophan.



(XXXV.)

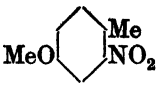
The removal or partial removal of the methyl group at the high temperature of a zinc-dust distillation is not without precedent, and it may be recalled that *N*-methyldiphenylamine, Ph·NMe·Ph, yields carbazole and not methylcarbazole by pyrogenic decomposition (Gräbe, *Annalen*, 1874, **174**, 181). The other products of the reaction were hydrogen, nitrogen, methane, benzene, aniline, benzonitrile, and diphenylamine.

This synthesis of norharman affords direct and independent confirmation of the correctness of the constitution assigned to harmine so far as the nuclear ring system is concerned. Further, the position of the methyl group is placed beyond doubt by a comparison of the reactions whereby norharman and harman are obtained from tryptophan. Synthetical evidence in regard to the position of the methoxyl group is alone lacking, and we are continuing our experiments in this direction, some progress having already been made. In the first place, 6-methoxyindole-2-carboxylic acid (XXXVI) has been synthesised in some quantity by the following series of reactions. *o*-Nitro-*p*-tolyl methyl ether (XXXVII), obtained by the methylation of *o*-nitro-*p*-cresol with methyl sulphate, on treatment with ethyl oxalate in the presence of alcoholic sodium ethoxide, yields o-*nitro*-p-*methoxyphenylpyruvic acid* (XXXVIII).

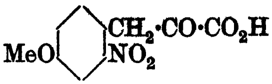
This interesting new acid is oxidised by hydrogen peroxide with formation of o-*nitro*-p-*methoxyphenylacetic acid* (m. p. 158°), and this is reduced by zinc dust and acetic acid with formation of o-*azoxy*-p-*methoxyphenylacetic acid*,

$$CO_2H{\cdot}CH_2{\cdot}C_6H_3(OMe){\cdot}NO{:}N{\cdot}C_6H_3(OMe){\cdot}CH_2{\cdot}CO_2H,$$

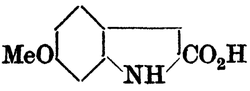
(m. p. 174°). On reduction with ferrous hydroxide, *o*-nitro-*p*-methoxyphenylpyruvic acid is converted in good yield into 6-methoxyindole-2-carboxylic acid (m. p. 197°), and this acid loses carbon dioxide on heating with production of 6-*methoxyindole* (m. p. 92°) (XXXIX), a new member of the little investigated series of the alkyloxyindoles and one of the parent substances of harmine and harmaline.



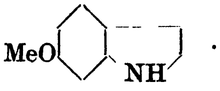
(XXXVII.)



(XXXVIII.)

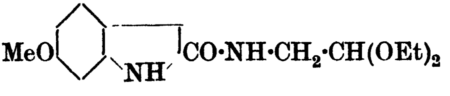


(XXXVI.)

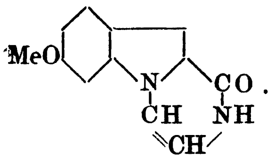


(XXXIX.)

The chloride of 6-methoxyindole-2-carboxylic acid reacts normally with aminoacetal, yielding 6-methoxyindole-2-carboxyacetalylamide (m. p. 123°) (XL), and this on treatment with alcoholic hydrochloric acid is readily converted into 11-methoxy-5-keto-4 : 5-dihydroindolediazine (1 : 4) (XLI).



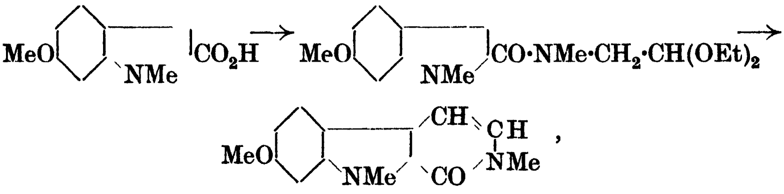
(XL.)



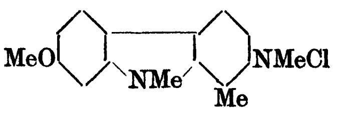
(XLI.)

This substance melts at 253° and closely resembles in appearance and properties 5-keto-4 : 5-dihydroindolediazine (1 : 4) (XV).

Experiments are in progress which have for their object the preparation of the following series of substances :

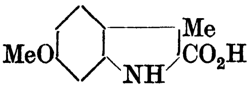


the latter of which is particularly interesting on account of its close relation to harmine and it is hoped that it may be converted into dimethylharmine chloride (XLII) by the action of magnesium methyl iodide followed by treatment with hydrochloric acid.

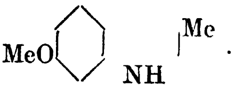


(XLII.)

The starting point in this series of reactions will no doubt be most readily obtained from *m*-methoxyphenylmethylhydrazine, $MeO·C_6H_4·NMe·NH_2$, by an application of E. Fischer's synthesis of indole derivatives, and it is therefore of considerable interest that the results incidentally obtained in the course of our experiments go to show that such a synthesis is likely to be successful and that the groups in the benzene nucleus will have the desired orientation. This follows from the identity of the methoxyscatole, which is obtained by the two methods described below. The product of the condensation of *o*-nitro-*p*-tolyl methyl ether and ethyl oxalate in alcoholic sodium ethoxide (*vid. supra*) was directly methylated by means of methyl iodide and subsequently reduced by means of zinc and acetic acid. In this way a good yield of ethyl 6-methoxy-3-methylindole-2-carboxylate (m. p. 128°) is obtained, and from this the 6-methoxy-3-methylindole-2-carboxylic acid (XLIII) is produced by hydrolysis. This methoxyscatolecarboxylic acid melts at 202° with evolution of carbon dioxide and formation of 6-methoxy-3-methylindole (XLIV) or 6-methoxyscatole (m. p. 125°).



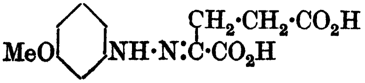
(XLIII.)



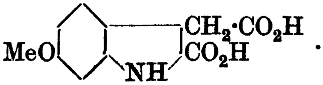
(XLIV.)

In order to enlarge the basis of synthetical operations in the methoxyindole group, it was considered highly desirable to investigate the behaviour of a suitable *m*-methoxyphenylhydrazone, and it became necessary to devise a method for the preparation of *m*-methoxyphenylhydrazine, $MeO \cdot C_6H_4 \cdot NH \cdot NH_2$, an interesting substance which does not appear to have been described. The base was made in considerable amount from *m*-anisidine by the usual process of diazotisation in hydrochloric acid and reduction with stannous chloride. It distils at 168°/15 mm., solidifying in a freezing mixture, and its stability is remarkable when compared with that of the corresponding *o*- and *p*-derivatives. The methoxyl group in the *ortho*- or *para*-position enormously increases the ease with which the hydrazine is reduced to the related aniline derivative and ammonia, but this effect is evidently unimportant when the methoxyl is in the *meta*-position.

m-Methoxyphenylhydrazine condenses readily with α-keto-glutaric acid, and if the product (XLV) is dissolved in alcohol and the solution saturated with hydrogen chloride, 6-methoxy-2-carboxyindole-3-acetic acid (XLVI) is directly produced.



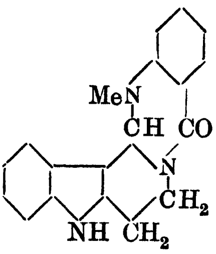
(XLV.)



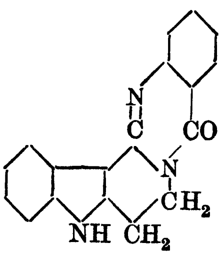
(XLVI.)

This acid will serve as the basis for a number of experiments which we hope to carry out. It melts at 225° and decomposes smoothly with formation of 6-methoxyscatole identical with the substance obtained as described above from *o*-nitro-*p*-tolyl methyl ether by a series of reactions. The important point is thus established that indole-ring formation in the case of a *m*-methoxyphenylhydrazone takes place in the *para*-position with respect to the methoxyl group.

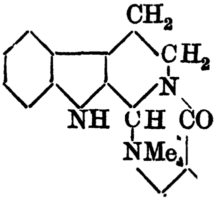
In view of the fact that tryptophan, aribine (loturine), harmine, and harmaline undoubtedly contain a —C—C—N— chain attached to the 3-position in indole, it would be highly remarkable and surprising if there should exist a series of naturally occurring substances in which a similar chain is attached to the 2-position, although it would, of course, be most unwisely dogmatic to deny the possibility of this. In the case of the alkaloids of *Evodia rutæcarpa*, the brilliant work of Asahina and Mayeda (*J. Pharm. Soc. Japan*, 1916, No. 416; consulted only in an abstract, A., 1921, **120**, i, 48) has led to the adoption by these authors of the formulæ XLVII and XLVIII for evodiamine and rutæcarpine respectively, and it will not be out of place to examine the validity of the evidence which rules out the constitutions which would bring these bases into line with the tryptophan group, for example, the expression XLIX for evodiamine.



(XLVII.)

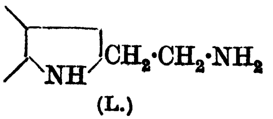


(XLVIII.)



(XLIX.)

Evodiamine is hydrolysed, first by alcoholic hydrochloric acid and then by alcoholic potassium hydroxide, with the formation of a base, $C_{10}H_{12}N_2$, to which the constitution L is assigned,



,

(L.)

and this is the crux of the whole matter. A portion of the evidence, at any rate, is likely to prove fallible, since one of the arguments adduced is to the effect that this base yields indole-2-carboxylic acid on fusion with potassium hydroxide. Now whilst 2-methylindole yields indole-2-carboxylic acid on fusion with potassium hydroxide, it is also true that even such a simple 3-substituted indole as scatole yields some indole-2-carboxylic acid mixed with indole-3-carboxylic acid when submitted to similar treatment (Ciamician and Zatti, *Ber.*, 1888, **21**, 1933). The sole product from the alkali fusion of tetrahydrocarbazole was indole-2-carboxylic acid (Zanetti, *Ber.*, 1893, **26**, 2007). The longer the sidechain of a 3-substituted indole the more numerous will be the opportunities for side-reactions and formation of cyclic structures, and consequently the greater the probability that indole-2-carboxylic acid would result from the vigorous process of fusion with potassium hydroxide. We are inclined to discount the value of this evidence, since the production of indole-2-carboxylic acid would be in harmony with either of the possible views of the nature of the aminoethylindole from evodiamine. A much more serious difficulty is found in the fact that the base melts at 120° (*N*-benzoyl derivative, m. p. 173—174°), whereas 3-β-aminoethylindole, synthesised by Ewins (T., 1911, **99**, 270), melts at 145—146° (*N*-benzoyl derivative, m. p. 137—138°). This is apparently conclusive, but there is just the possibility of a loop-hole, such as the existence of the base in polymorphic forms, and the matter is of such interest that it is proposed to attempt an independent synthesis of 3-β-aminoethylindole, not only with the object indicated above, but also because this base is a very suitable starting point for syntheses in the harmine group.

EXPERIMENTAL.

Harman from Tryptophan.

In Part IV (T., 1919, **115**, 968) of this investigation it was proved that the base, $C_{12}H_{10}N_2$, obtained by Hopkins and Cole (*J. Physiol.*, 1903, **29**, 451) by the oxidation of tryptophan with ferric chloride is identical with harman, and the mechanism of the reaction has engaged our attention. A small yield of harman was obtained by following out precisely the directions given by Hopkins, but the result was negative when precautions were taken to exclude alcohol and ether. Professor Hopkins has kindly informed us that in his own experience the results of the oxidation have been variable and yields varying from nothing to more than 30 per cent. of the theory have been obtained, and suggests that the C_2-group may possibly arise from the ether used to extract the indolealdehyde, which is the second product obtained in the reaction, especially since the oxidation mixture was allowed to remain over-night in contact with the solvent. Harman may also be obtained from tryptophan by the following processes.

(*A*) Tryptophan (1 gram) was dissolved in water (250 c.c.) to which sulphuric acid (1 c.c.) and then acetaldehyde (10 c.c. of 20 per cent. aqueous solution) was added. The liquid was boiled during ten minutes, the source of heat removed, and a 10 per cent. aqueous solution of potassium dichromate (50 c.c.) slowly added while the mixture was still hot. After allowing to remain for five minutes, the solution was heated to boiling and then allowed to cool. The excess of oxidising agent was reduced by sulphurous acid and the chromium precipitated by means of sodium carbonate in boiling solution, the faintly alkaline liquid was then filtered and the precipitate washed with boiling water. The combined filtrate and washings were acidified by addition of hydrochloric acid, boiled with animal charcoal, again filtered, and evaporated to a small bulk on the steam-bath. The base was precipitated by the addition of concentrated aqueous sodium hydroxide, collected, washed with water, and dried in a vacuum. The yield was 0·2 gram. After two crystallisations from benzene, the substance was obtained in nearly colourless prisms melting at 237—238°, and at the same temperature when mixed with a specimen of pure harman.

(*B*) Tryptophan (3 grams) was heated with acetic anhydride (20 c.c.) until dissolved, zinc chloride (2 grams) was then added and the mixture boiled during one minute. Decomposition of the excess of acetic anhydride by the addition of hot water (150 c.c.) led to the separation of a brown oil, which was converted into a yellow, sparingly soluble chromate by aqueous potassium dichromate (60 c.c. of 10 per cent. solution) to which concentrated sulphuric acid (3 c.c.) had been added. The solid was well broken up and the mixture boiled until nearly the whole of the chromate had passed into solution, a stage reached after about twenty minutes. Excess of sodium hydroxide was added and the base extracted by means of ethyl acetate. The ethyl acetate solution was washed with a little water and then with dilute hydrochloric acid. The acid washings were concentrated and on treatment with alkali yielded 0·5 gram of harman, which was crystallised and identified as in the previous example.

(*C*) Harman was obtained from tryptophan in small yield in various ways, of which the most interesting is the simultaneous oxidation of alanine and tryptophan by means of chromic acid in dilute solution. Tryptophan (1 gram) and alanine (2 grams) dissolved in boiling dilute sulphuric acid (250 c.c.; 0·5 per cent.) were oxidised by the slow addition of potassium dichromate (5 grams) dissolved in water (100 c.c.). The product was worked up as in (*A*) above and a small yield of harman obtained.

Attempts were made to produce harman by applying to tryptophan a process similar to that which is used for the conversion of diacetonamine oxalate into vinyldiacetonamine oxalate. When tryptophan was boiled with butyl alcohol, oxalic acid, and acetal a brownish-yellow solution exhibiting green fluorescence was obtained. On extraction with dilute sulphuric acid, a solution exhibiting bluish-violet fluorescence was produced, and the reactions of the base which could be obtained from this by treatment of the concentrated liquid with alkali were not those of harman but more nearly resembled those of an alkylated harman. A small amount of *harman butyl iodide* was prepared, and the colour and fluorescence changes in acid, neutral, and alkaline solution were identical with those of the product in the above experiment. A complete examination of the reaction would be of interest, but the amount of tryptophan at our disposal did not permit of this.

Harmolic Acid.

Norharmolcarboxylic Acid (Formula III).

The fusion of harmol with potassium hydroxide was carried out exactly as described by O. Fischer (*Ber.*, 1889, **22**, 642) and the isolation of the acid by fractional acidification of the dissolved melt with sulphuric acid was also effected. The crystallised product gave on analysis numbers agreeing closely with those determined by Fischer, namely C = 55·5; H = 3·7; N = 10·8; as against C = 55·6, 55·2; H = 3·8, 3·7; N = 11·1, 11·4 per cent., as given by Fischer. On the basis of these results, Fischer (*loc. cit.*) suggested the formula $C_{12}H_{10}O_5N_2$, which is extremely difficult to explain if the constitution of harmine now adopted by the present authors is correct.

In view of the relatively sharp melting point of the product (247°), the problem appeared rather puzzling until the presence of sulphur was established (Found: S = 4·0 per cent.).

The harmolic acid of O. Fischer therefore appears to be a *sulphate* of *norharmolcarboxylic acid* of the composition $(C_{12}H_8O_3N_2)_3,H_2SO_4$, requiring C = 55·2; H = 3·3; N = 10·7; S = 4·1 per cent.

The acid itself is readily obtained by dissolving this curious sulphate in dilute ammonia and precipitating from the filtered hot solution by addition of acetic acid. The very pale yellow powder was well washed with hot water and dried at 140°. It could not be crystallised on account of its extremely sparing solubility in organic solvents, but prepared from pure " harmolic acid " it is practically homogeneous and melts with much frothing and decomposition at 272° after darkening at 267° (Found: C = 63·3; H = 3·6; N = 12·6. $C_{12}H_8O_3N_2$ requires C = 63·1; H = 3·5; N = 12·4 per cent.). The substance is readily soluble in alkalis, and the solutions couple with diazo-salts, forming orange-red azo-derivatives. The compound is also feebly basic, forming yellow salts with mineral acids.

Norharmol (Formula IV).

This substance is the phenolic base which O. Fischer obtained by heating harmolic acid (*loc. cit.*), and to which he ascribed the composition $C_{11}H_{10}ON_2$. We have obtained the compound by heating pure norharmolcarboxylic acid with glycerol until carbon dioxide was no longer evolved and a clear solution was obtained. On cooling, norharmol separated in nearly colourless needles and was washed with aqueous alcohol and then with alcohol and dried at 140° (Found: C = 71·5; H = 4·6; N = 15·2. $C_{11}H_8ON_2$ requires C = 71·7; H = 4·3; N = 15·2 per cent.).

On heating, the substance sublimes in small needles.

It is soluble in caustic alkalis, but not in sodium carbonate or ammonia, and in alkaline solution it exhibits blue fluorescence and couples with diazo-salts. It is a base dissolving in dilute acids to yellow solutions. The platinichloride was analysed by O. Fischer (*loc. cit.*) and with results agreeing with the composition now suggested.

Conversion to Norharmine.—Norharmol (0·5 gram) was heated in a sealed tube at 150° with water (25 c.c.), methyl alcohol (10 c.c.), sodium hydroxide (1 gram), and potassium methyl sulphate (3 grams) for three hours. After adding excess of sodium hydroxide, the contents of the tube were extracted with much ether and the ethereal solution was washed with water and dried by potassium hydroxide. After removal of the solvent, a residue was obtained which could be crystallised from benzene in colourless needles melting at 218°, alone or mixed with a specimen of pure norharmine (Perkin and Robinson, T., 1912, **101**, 1775).

Norharman (*4-Carboline*) (Formula II).

(*A*) Norharmol (5 grams) was mixed with zinc dust (100 grams) and carefully distilled in accordance with the usual technique of the operation in a stream of hydrogen, the vapours being passed over a further large amount of zinc dust. The product was converted into the nitrate and this salt crystallised from hot dilute nitric acid. The base was then precipitated by the addition of sodium hydroxide to an aqueous solution of the purified nitrate, collected, and crystallised from benzene.

(*B*) Harman (3 grams) was boiled during an hour with pure benzaldehyde (10 c.c.), when the liquid became yellow and water was eliminated. The product was mixed with ether and shaken with hydrochloric acid (10 c.c. of concentrated acid and 15 c.c. of water), when a bright yellow hydrochloride separated. This was collected and washed with ether. The substance is undoubtedly *benzylideneharman hydrochloride*, and is very similar in appearance and properties to the analogous harmine derivative (Perkin and Robinson, *loc. cit.*). When it is treated in alcohol with ammonia, a pale yellow solution is obtained which exhibits a most striking violet fluorescence. The whole of the hydrochloride was dissolved in pure pyridine (20 c.c.) and oxidised by means of a cold saturated solution of potassium permanganate until a pink coloration remaining permanent for an hour was obtained. The excess of permanganate was reduced by warming with a few drops of alcohol and the filtered solution evaporated to a small bulk and mixed with excess of hydrochloric acid. The yellow precipitate was collected and dissolved in the least amount of hot dilute ammonia and acidified with acetic acid. The pale yellow precipitate was collected, washed with hot water, and dried at 100°. It was then heated in a test-tube with a little glycerol until carbon dioxide ceased to be evolved and the glycerol boiled. The product was mixed with water and picric acid added. The bright yellow picrate was collected, washed, and at once decomposed by ammonia in presence of a considerable volume of warm benzene. The separated solution was washed with aqueous sodium hydroxide and dried by solid potassium hydroxide, and after filtration the greater part of the benzene was removed by distillation. The crystals which separated were again crystallised from benzene.

(*C*) Of the various sets of conditions tested for the conversion of tryptophan into norharman the following gave the most satisfactory results. A mixture of tryptophan (3 grams), water (250 c.c.), sulphuric acid (2 c.c.), and aqueous formaldehyde (5 c.c. of 35 per cent.), added in the order named, was boiled during one minute, the lamp removed, and aqueous potassium dichromate (200 c.c. of 10 per cent.) added and the liquid allowed to cool. Excess of sodium hydroxide was added and the liquid extracted several times with ethyl acetate. The extract was washed with a little dilute sodium hydroxide and then with dilute hydrochloric acid, and it is necessary to do this repeatedly, as norharman hydrochloride is to some extent soluble in ethyl acetate. The combined acid solutions were boiled with animal charcoal, filtered, and evaporated to a small bulk. The base was then precipitated by the addition of excess of sodium hydroxide and collected. The yield was 0·9 gram, which is 36 per cent. of that demanded by theory. The substance is best purified by crystallisation of the nitrate from dilute nitric acid (1 : 3), this salt being sparingly soluble in the cold and crystallising in slender, yellow needles. The regenerated base is then crystallised from a mixture of ethyl acetate and light petroleum (b. p. 60—70°), and finally from benzene and dried at 100° (Found: C = 78·4; H = 4·8; N = 17·0. $C_{11}H_8N_2$ requires C = 78·5; H = 4·8; N = 16·7 per cent.).

Norharman crystallises from benzene in colourless, slender needles and melts at 198·5°. It is sparingly soluble in cold benzene or light petroleum, moderately soluble in ether or ethyl acetate, and readily soluble in methyl or ethyl alcohol. It is fairly readily soluble in hot water and crystallises on cooling in woolly needles. In neutral solvents, its fluorescence is barely perceptible, but in dilute acid solution it exhibits a vivid blue fluorescence. The specimens of norharman prepared according to the methods *A* and *B* above melted at 197—198°, and mixed with the especially purified specimen obtained from tryptophan melted at the same temperature. Norharman does not exhibit numerous colour reactions. It gives no colour with a pine shaving, nor with *p*-dimethylaminobenzaldehyde and alcoholic hydrochloric acid. Neither does it show any sign of change in presence of vanillin and hydrochloric acid, although the similarly constituted carbazole gives a purple coloration with this reagent. Finally, it does not couple with diazonium salts. On reduction with sodium in boiling butylalcoholic solution, a substance is obtained which no longer exhibits fluorescence in acid solution. This product combines to some extent with *p*-nitrobenzenediazonium acetate to a reddish-brown azo-derivative, orange-red on the addition of hydrochloric acid.

The *mercurichloride* crystallises from hot dilute hydrochloric acid in yellow needles and is sparingly soluble.

The *picrate* crystallises from hot water in flocculent, intensely yellow needles melting at 260° with decomposition. It may also be conveniently crystallised from ethyl alcohol in slender needles. It is very sparingly soluble in cold water and alcohol and has frequently been employed as a means of recovering norharman from dilute solutions (Found: * N = 17·8. $C_{17}H_{11}O_7N_5$ requires N = 17·6 per cent.).

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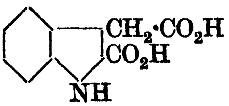
* Dried at 100°.

2-Carboxyindole-3-acetic Acid,



For the purposes of this research, this acid was prepared in quantity by a modification of the process of Wislicenus and Waldmüller (*Ber.*, 1911, **44**, 1572). α-Ketoglutaric acid (39·3 grams), dissolved in alcohol (300 c.c.), is mixed with a solution of phenylhydrazine (33 grams) in alcohol (200 c.c.) and then a stream of hydrogen chloride passed sufficiently rapidly to raise the alcohol to the boiling point. The liquid first darkens in colour, then becomes less coloured, and ammonium chloride separates. After heating under reflux for an hour, the ammonium chloride is filtered off, washed with alcohol, and the alcoholic hydrogen chloride removed by distillation under reduced pressure.

On the addition of water, the ethyl ester of 2-carboxyindole-3-acetic acid separates as a yellow syrup which soon solidifies and, after recrystallisation from a small quantity of alcohol, melts at 83—84°, as stated by Wislicenus and Waldmüller. In order to obtain the free acid, it is convenient to boil the crude ester with dilute sodium hydroxide (8 per cent.) for about two to three hours. After filtering from a small amount of black tar, the solution is acidified with dilute hydrochloric acid, when, on rubbing, 2-carboxyindole-3-acetic acid separates in small, brown crystals. For analysis, the acid was recrystallised from benzene (Found : C $=60·7$; $H = 4·5$. $C_{11}H_9O_4N$ requires $C = 60·3$; $H = 4·1$ per cent.).

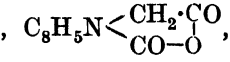
2-Carboxyindole-3-acetic acid melts at 235—236° and exhibits a marked tendency to form supersaturated solutions. It dissolves appreciably in boiling water and separates, on cooling and scratching, in minute white needles; in alcohol, it is readily soluble, but much less so in benzene, and is almost insoluble in light petroleum. The alcoholic solution, mixed with *p*-dimethylaminobenzaldehyde and a drop of hydrochloric acid, becomes reddish-blue on boiling and on cooling the colour largely fades, only a pale blue tint remaining. The deep reddish-blue colour develops again on boiling. The addition of a drop of sodium nitrite changes the cold, pale blue liquid to a deeper blue, which becomes still deeper on boiling. Heated in a test-tube, the acid decomposes with evolution of carbon dioxide, and the residue, boiled with very dilute sodium carbonate, deposits on cooling lustrous plates which melt at 95° and consist of scatole.

Dimethyl Ester of 2-Carboxyindole-3-acetic Acid, $C_8H_5N(CO_2Me)(CH_2{\cdot}CO_2Me)$.

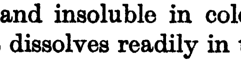
Considerable quantities of this methyl ester were prepared by employing methyl alcohol in the place of ethyl alcohol in the experiment described at the commencement of this section. Most of the methyl alcohol and hydrochloric acid was distilled from the product under reduced pressure, when, on standing, the dimethyl ester separated in green crystals, which were collected and washed with water to remove ammonium chloride. A further yield of less pure material was obtained by diluting the methyl-alcoholic mother-liquor with water, and both crops were purified by recrystallisation from methyl alcohol. The same substance was also obtained by esterifying 2-carboxyindole-3-acetic acid with methyl alcohol and hydrochloric acid in the usual manner (Found : C = 63·2 ; H = 5·3. $C_{13}H_{13}O_4N$ requires C = 63·1 ; H = 5·3 per cent.).

This *dimethyl* ester melts at 126—127°, is moderately readily soluble in boiling methyl alcohol, and separates in compact prisms. In general it is not so readily soluble in organic solvents as the diethyl ester.

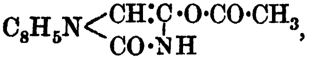
The alcoholic solution, containing *p*-dimethylaminobenzaldehyde and hydrochloric acid, gives on boiling a pale red coloration which becomes more intense on the addition of sodium nitrite.

The *anhydride*,  $C_8H_5N{<}\begin{matrix}CH_2{\cdot}CO\\ CO{-}O\end{matrix}$, is formed when the acid is heated with acetic anhydride, and the presence of acetyl chloride appears to improve the yield and the purity of the product. A mixture of freshly distilled acetic anhydride (100 grams) and acetyl chloride (10 grams) is added to the acid (20 grams) and the mixture heated gently, at first on the water-bath and then to boiling. The acid dissolves and, when the solution is almost boiling, a mass of crystals separates ; after standing for an hour, these are collected, washed with acetic anhydride, and dried at 100°. The yield is about 13 grams, and, for analysis, the anhydride was recrystallised from acetic anhydride (Found : C = 65·4 ; H = 4·1 ; N = 6·8. $C_{11}H_7O_3N$ requires C = 65·7 ; H = 3·5 ; N = 7·0 per cent.).

When rapidly heated, this anhydride begins to blacken at 230° and melts with decomposition at about 250°. It is very sparingly soluble in alcohol or ether and insoluble in cold dilute sodium carbonate or hydroxide, but it dissolves readily in the latter on boiling.

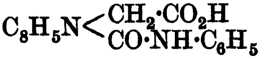
The Acid-amide,  $C_8H_5N{<}\begin{matrix}CH_2{\cdot}CO_2H\\ CO{\cdot}NH_2\end{matrix}$ (?).—With the object of obtaining the imide, the anhydride was dissolved in naphthalene at 180° and a current of carefully dried ammonia passed, when a white, sparingly soluble substance separated, which proved to be the amide. Benzene was added to dissolve the naphthalene, and the white powder collected and washed with benzene, when it was found that the substance was readily soluble in dilute sodium carbonate, and analysis proved that it was the amide figured above. The same substance was subsequently more conveniently prepared in the following manner : A mixture of the anhydride (10 grams) with solid ammonium acetate (50 grams) is melted and the melt boiled gently for half an hour. The clear liquid, on cooling and mixing with water and dilute hydrochloric acid, gradually deposits the amide as a green solid, which is purified by crystallisation from alcohol, from which it separates in colourless needles which melt at 242—244° with decomposition (Found : $C = 60{\cdot}9$; $H = 4{\cdot}6$; $N = 12{\cdot}2$. $C_{11}H_{10}O_3N_2$ requires $C = 60{\cdot}6$; $H = 4{\cdot}6$; $N = 12{\cdot}8$ per cent.). The solution of the amide in alcohol containing *p*-dimethylaminobenzaldehyde and hydrochloric acid gives, on boiling, a purple blue coloration which fades somewhat on cooling. The addition of a drop of sodium nitrite in the cold changes the colour, and a peculiar dichroic liquid is obtained which is garnet-red to transmitted and blue to reflected light.

Many experiments were made with this amide in the hope that it might be found possible to convert it into the imide (compare p. 1605). When the amide is heated in a test-tube, decomposition readily sets in and an odour reminiscent of scatole develops, but no imide appears to be formed.

Similarly, the imide was not obtained when the di-ammonium salt of 2-carboxyindole-3-acetic acid was heated. The next attempt to obtain the imide was by heating the amide with acetic anhydride and acetyl chloride. When the amide was gently warmed on the water-bath with acetic anhydride (10 c.c.) and acetyl chloride (2 c.c.), it passed into solution, and, on further heating, the whole soon became semi-solid owing to the separation of a colourless, crystalline substance. After cooling, this was collected and recrystallised from acetic acid, from which it separated in minute, colourless needles which melted, with decomposition, at about 312°. This characteristic substance is insoluble in sodium carbonate or hydroxide in the cold, but dissolves in 12 per cent. sodium hydroxide, on gently warming, to a yellowish-green solution (Found : $C = 64{\cdot}3$; $H = 4{\cdot}0$; $N = 11{\cdot}3$. $C_{13}H_{10}O_3N_2$ requires $C = 64{\cdot}5$; $H = 4{\cdot}1$; $N = 11{\cdot}6$ per cent.). This analysis indicates that the substance is an acetyl derivative of the imide of the probable constitution  $C_8H_5N{<}\begin{array}{l}CH{:}C\cdot O\cdot CO\cdot CH_3\\ CO\cdot NH\end{array}$, but so far we have not been successful in removing the acetyl group and obtaining the imide itself.

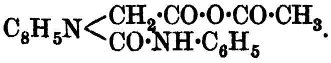
Similar want of success attended a series of experiments on the action of ammonia on the dimethyl ester of 2-carboxyindole-3-acetic acid (p. 1623). If the dimethyl ester is heated in a sealed tube with methyl alcohol saturated with ammonia at 0°, no crystalline substance separates, and, on opening the tube, a deep green colour develops on the surface and the liquid stains the skin.

The Anilide,



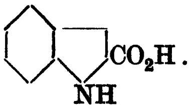
$C_8H_5N<\begin{matrix}CH_2\cdot CO_2H\\ CO\cdot NH\cdot C_6H_5\end{matrix}$ (?).—This derivative was prepared by boiling for fifteen minutes a mixture of aniline (5 grams), acetic acid (5 grams), and the anhydride of the acid (2 grams; p. 1623). On mixing the product with dilute hydrochloric acid, a green slime of crystals, containing acetanilide, separated, and these were collected and extracted with dilute ammonia. The alkaline extract was precipitated by hydrochloric acid, and the crystals, which were still sticky, were dissolved in sodium carbonate and again precipitated with hydrochloric acid. The voluminous mass of colourless crystals (2 grams) was collected, washed with water, and recrystallised from alcohol, from which the substance separated in needles melting at 216—217° (Found: C = 69·6; H = 5·0. $C_{17}H_{14}O_3N_2$ requires C = 69·4; H = 4·8 per cent.). When this anilide (1·6 grams) was warmed with acetic anhydride (10 c.c.) and acetyl chloride (1·5 c.c.), it dissolved, and, on cooling, crystals separated which, after washing with alcohol and crystallising from acetic anhydride, melted at 182° (Found: C = 67·8; H = 4·8; N = 8·2. $C_{19}H_{16}O_4N_2$ requires C = 67·8; H = 4·8; N = 8·3 per cent.).

This substance is insoluble in dilute sodium carbonate or hydroxide and evidently corresponds with the mixed anhydride of the anilide of 2-carboxyindole-3-acetic acid and acetic acid. Its constitution is probably that represented by the formula



$C_8H_5N<\begin{matrix}CH_2\cdot CO\cdot O\cdot CO\cdot CH_3\\ CO\cdot NH\cdot C_6H_5\end{matrix}.$

Indole-2-carboxylic Acid,



This acid, which we required in considerable quantities, was, in the first instance, prepared from pyruvic acid and phenylhydrazine by the method discovered by E. Fischer (*Annalen*, 1866, **236**, 142). Subsequently, a modification of the process described by Reissert (*Ber.*, 1897, **30**, 1030) was worked out, which was found to be convenient, and is briefly as follows:—*o*-Nitrophenylpyruvic acid, $NO_2\cdot C_6H_4\cdot CH_2\cdot CO\cdot CO_2H$ (20·9 grams), prepared as described by

Reissert, is dissolved in ammonia (140 c.c. of *d* 0·880 diluted with 200 c.c. of water), a hot solution of crystallised ferrous sulphate (180 grams in 200 c.c. of water) gradually added, and the whole first warmed on the water-bath for half an hour and then boiled for the same time. After filtering, the filtrate and washings of the ferric oxide are concentrated considerably and acidified, when indole-2-carboxylic acid separates in the form of a white, crystalline powder, which, after remaining over-night, is collected, washed with cold water, and dried in the steam-oven. In this condition the acid is nearly pure, melts at 202—204°, and the yield is 12—13 grams, or about 70 per cent. of theory.

On heating in alcoholic solution with *p*-dimethylaminobenzaldehyde and hydrochloric acid, indole-2-carboxylic acid develops a red coloration, which fades on cooling and returns again on boiling.

Indole-2-carboxyacetalylamide (Formula XIII).

As stated in the introduction, this substance is produced when aminoacetal reacts with indole-2-carboxylic chloride. The preparation of this acid chloride was found to be a matter of some difficulty, but ultimately the following procedure led to the desired result.

Indole-2-carboxylic acid (3·2 grams), thoroughly dried, powdered, and passed through a fine sieve, is placed in a small fractionating flask, mixed with freshly distilled acetyl chloride (35 grams), and then powdered phosphorus pentachloride (4·2 grams) gradually added to the suspension, the whole being well cooled during the addition. The flask is removed from the ice and gently warmed by the heat of the hand until the pentachloride has disappeared. After remaining at the ordinary temperature for four hours, the flask is connected with the pump, and the acetyl chloride and phosphoryl chloride are removed by warming in water at about 40°, and finally at 50—55°. The residual acid chloride, although somewhat brown, is pure enough for the next operation, which is carried out as follows. The acid chloride is dissolved in warm dry chloroform (30 c.c. distilled over phosphoric oxide), the solution filtered rapidly from a little brownish-red impurity, cooled, and then aminoacetal (5·4 grams) dissolved in dry chloroform (10 c.c.) added, the vigorous reaction being controlled by careful cooling. After fifteen minutes, the flask is removed from the ice and salt, the chloroform distilled off under reduced pressure, the residue mixed with water, the crystalline precipitate collected with the aid of the pump, and dried on porous porcelain in a vacuum desiccator. The yield is about 80 per cent. of theory, and the substance, in this condition, melts at 131—132° and is almost pure. For analysis it was crystallised from alcohol (Found: C = 65·5; H = 7·3; N = 10·4. $C_{15}H_{20}O_3N_2$ requires C = 65·2; H = 7·2; N = 10·2 per cent.).

Indole-2-carboxyacetalylamide melts at 133°, is readily soluble in alcohol, but less so in benzene, and crystallises from either solvent in small, colourless needles. It is very readily soluble in ether, but sparingly so in light petroleum. It decomposes gradually at 100°, turning yellow and giving off alcohol, and this decomposition takes place rapidly at about 140°. In a quantitative experiment carried out under these conditions, it was found that the acetal lost 26·7 per cent. of alcohol, whereas the elimination of one molecule of alcohol corresponds with 16·7 and that of two molecules with 33·3 per cent. loss. The residue is a hard, brittle mass sparingly soluble in most neutral organic solvents. It dissolves in hot acetic acid, but does not separate on cooling, and the addition of water precipitates an amorphous powder, which was not further investigated.

5-*Keto*-4 : 5-*dihydroindolediazine* (1 : 4) (Formula XV).

When indole-2-carboxyacetalylamide (2 grams) is added to a saturated solution of hydrogen chloride in alcohol at 40—45°, it soon dissolves to a deep yellowish-brown solution, and in a few minutes yellow crystals separate. After half an hour, the crystals are collected with the aid of the pump and recrystallised from boiling alcohol, in which the substance is sparingly soluble and from which it separates in short, yellow needles melting at 247° (Found: C = 72·2; H = 4·7; N = 14·9. $C_{11}H_8ON_2$ requires C = 71·7; H = 4·3; N = 15·2 per cent.). The bright yellow solution of this compound in ethyl alcohol fluoresces green, but the addition of a drop of concentrated aqueous potassium hydroxide produces a duller yellow liquid which exhibits bluish-violet fluorescence, and the reaction is evidence of the phenolic (enimic) character of this cyclic amide. That it contains a free position in the pyrrole nucleus is very probable in view of the following observations. A pine shaving is coloured a weak mauve-red by a hot alcoholic hydrochloric acid solution of the substance. When an alcoholic solution is heated with an equal volume of concentrated hydrochloric acid and a trace of *p*-dimethylaminobenzaldehyde added, a green coloration which becomes blue on the addition of water is obtained. The addition of vanillin to a suspension of the compound in concentrated hydrochloric acid causes a reddish-purple coloration even in the cold. On warming, this becomes very intense, and on the addition of water a purple precipitate is thrown down. Addition of sodium hydroxide causes a colour change through blue and green to yellow. *p*-Nitrobenzenediazonium chloride to which sodium acetate in excess is added gives with an alcoholic solution of the substance a yellow colour changing to orange and reddish-brown and finally a reddish-brown precipitate of an azo-derivative. In presence of sodium hydroxide, the coupling occurs immediately to a deep bordeaux-red solution, and the reddish-brown precipitate is obtained on acidification. On boiling the substance (m. p. 247°) with concentrated hydrochloric acid, the initially clear yellow solution clouds at a certain stage and becomes faintly green. The crystalline material in suspension becomes viscous, and on the addition of water a sulphur-yellow material is precipitated. The reaction suggests polymerisation and instability to vigorous treatment with acids. No doubt the very unusual constitution of this compound would modify the indole colour reactions to a considerable extent, and tests were therefore also applied to a reduction product which can be obtained by the action of an excess of sodium in boiling butyl alcohol. The pine-shaving reaction was mauve-red, and stronger than with the original substance. The dimethylaminobenzaldehyde reaction was rose-red, the vanillin–hydrochloric acid reaction was bright red, changing to purple on heating, whilst the coupling with *p*-nitrobenzenediazonium acetate gave a brownish-red as before, but the azo-derivative was in this case an indicator, and changed to crimson on the addition of hydrochloric acid. At an early stage of this investigation, it was thought that this substance might be a derivative of 4-carboline, and attempts were made in various directions to convert it into norharman, but uniformly without success. The products of distillation with zinc dust are indole and an orange base which sublimes readily and dissolves in dilute acids to an intense orange-yellow solution. This interesting substance could not be obtained in sufficient amount for examination. It may also be mentioned that the action of magnesium methyl iodide on the compound (m. p. 247°) in benzene solution results in the production of a base which fluoresces violet in ethyl acetate solution, but does not exhibit fluorescence in aqueous acid solution, a behaviour which is the reverse of that of harman.

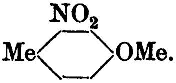
Condensation of Indole-2-carboxylic Chloride with Alanine Ester and with the Sodium Derivative of Ethyl Acetoacetate.

Indole-2-carboxy-α-(carbethoxy)ethylamide, $C_8H_6N{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2Et$. —This substance was readily obtained by the mixing of the acid chloride from 1·6 grams of indole-2-carboxylic acid (p. 1626) with a chloroform solution of alanine ester (2·4 grams), when a colourless, crystalline substance soon separated. This (1·4 grams) was collected, washed with chloroform, and dried in a vacuum desiccator over sulphuric acid, when it melted at 202° (Found: C = 64·4; H = 6·2. $C_{14}H_{16}O_3N_2$ requires C = 64·6; H = 6·2 per cent.).

β-*Carbethoxy*-α-*methylvinyl Indole*-2-*carboxylate*,
$C_8H_6N{\cdot}CO{\cdot}O{\cdot}CMe{:}CH{\cdot}CO_2Et$ (?).
—The interaction of indole-2-carboxylic chloride with the sodium derivative of ethyl acetoacetate was studied in the hope that the product, on hydrolysis, might yield 2-acetylindole, $C_8H_6N{\cdot}CO{\cdot}CH_3$, but apparently it is formed by the interaction of the acid chloride with the enol modification of ethyl acetoacetate. Indole-2-carboxylic acid (3·2 grams) was converted into the acid chloride in the usual manner (p. 1626), and the latter, dissolved in ether, added to an alcoholic solution of the sodium derivative of ethyl acetoacetate prepared from sodium (1 gram) and ethyl acetoacetate (5·2 grams). As there was little apparent change after twenty-four hours, the ether was slowly distilled off and the alcoholic solution heated on the steam-bath for half an hour. On adding water, a rather dark, semi-solid mass separated, which was collected, washed, and crystallised first from alcohol and then from benzene (Found: C = 66·0; H = 5·3. $C_{15}H_{15}O_4N$ requires C = 65·9; H = 5·5 per cent.).

This substance melts at 101°, is insoluble in dilute sodium hydroxide, and gives, in alcoholic solution with ferric chloride, only a faint green coloration. It therefore appears likely that it has the constitution assigned to it above.

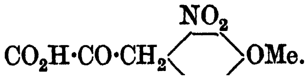
o-*Nitro*-p-*tolyl Methyl Ether*,



This substance may be readily obtained from *o*-nitro-*p*-tolyl carbonate (Friedlander, "Fortschritte der Theerfarben Fabrikation," Vol. **9**, p. 151) by hydrolysing with excess of sodium hydroxide solution and adding to the well-cooled product methyl sulphate and sufficient sodium hydroxide.

A better plan is to precipitate the *o*-nitro-*p*-cresol from the alkaline solution, obtained by the hydrolysis of the carbonate, by hydrochloric acid, to collect this with the aid of the pump, dry on porous porcelain and then methylate in the following way. Sodium (2 mols.), dissolved in the minimum quantity of methyl alcohol, is added to the solution of *o*-nitro-*p*-cresol (1 mol.) in methyl alcohol, the whole well cooled, and then methyl sulphate (1 mol.) added slowly with shaking and cooling. The product is warmed on the water-bath for half an hour, cooled, the sodium sulphate filtered off, and washed with a little methyl alcohol. The methyl alcohol is distilled off under reduced pressure, water added, and the crude methyl ether extracted with benzene and then the benzene solution extracted with dilute sodium hydroxide. After drying over calcium chloride and distilling off the benzene, the *o*-nitro-*p*-tolyl methyl ether is distilled under reduced pressure; it boils constantly at 150°/20 mm. The yield approximates to the theoretical.

o-*Nitro*-p-*methoxyphenylpyruvic Acid*,



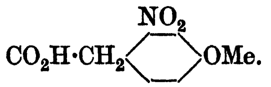
$CO_2H{\cdot}CO{\cdot}CH_2{\cdot}C_6H_3(NO_2){\cdot}OMe$.

In preparing this acid, sodium (9·2 grams), dissolved in alcohol (92 grams), was cooled and gradually mixed with ethyl oxalate (29·2 grams). *o*-Nitro-*p*-tolyl methyl ether (16·6 grams) was then added and the mixture kept at 35—40° in a thermostat for three days. The dark reddish-brown, gelatinous mass was cooled in ice, decomposed by the calculated amount of a mixture of equal weights of concentrated hydrochloric acid and ice and most of the alcohol distilled off from the water-bath under reduced pressure. The salt which had separated was removed with the aid of the pump, washed with ether, and the liquid extracted with ether until the extract was scarcely coloured red by the addition of sodium hydroxide. The ethereal solution was repeatedly shaken with dilute sodium hydroxide (5 per cent.), when, on acidifying the alkaline extract, crude *o*-nitro-*p*-methoxyphenylpyruvic acid separated and was extracted with ether. On standing, the ethereal solution deposited a small quantity of a substance very sparingly soluble in ether; this was removed by filtration and the ethereal solution dried and concentrated.

On adding benzene, the new acid gradually separated in a crystalline condition and was recrystallised from benzene, from which it separated in well-developed, yellow needles. These crystals contain benzene of crystallisation, melt at about 80°, but when heated rather below this temperature they become opaque and the melting point is then 144—145°. The loss in weight was found to be only 7·5 per cent., corresponding with the formula $4C_{10}H_9O_6N,C_6H_6$, which contains 7·5 per cent. of benzene (Found: in material heated at 80—90° until the weight was constant, C = 50·3; H = 3·9; N = 5·8. $C_{10}H_9O_6N$ requires C = 50·2; H = 3·8; N = 5·8 per cent.).

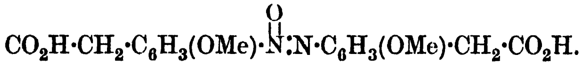
o-*Nitro*-p-*methoxyphenylpyruvic acid* is readily soluble in ether, alcohol, or acetic acid, but sparingly so in benzene. It dissolves appreciably in boiling water, and separates, on cooling, in pale greenish-yellow needles. Sodium hydroxide dissolves it with a deep purplish-red coloration. It reacts with phenylhydrazine, yielding a substance which melts at about 157°, but this has not been further investigated.

o-*Nitro*-p-*methoxyphenylacetic Acid*,



This acid is readily obtained under the following conditions: *o*-Nitro-*p*-methoxyphenylpyruvic acid, dissolved in the minimum amount of sodium hydroxide (2 per cent.), is cooled in ice-water and hydrogen peroxide solution slowly added until a test portion gives only a faint red coloration with sodium hydroxide. On acidifying, *o*-nitro-*p*-methoxyphenylacetic acid is precipitated as a sandy powder and may be recrystallised from 50 per cent. acetic acid, from which it separates in yellow needles. It melts at 157—158° and decomposes vigorously when it is heated, a fact which rendered analysis difficult (Found: N = 7·1. $C_9H_9O_5N$ requires N = 6·7 per cent.).

o-*Azoxy*-p-*methoxyphenylacetic Acid*,



$$CO_2H{\cdot}CH_2{\cdot}C_6H_3(OMe){\cdot}\overset{O}{N}{:}N{\cdot}C_6H_3(OMe){\cdot}CH_2{\cdot}CO_2H.$$

Reissert (*Ber.*, 1909, **41**, 3924), in describing his experiments on the reduction of *o*-nitrophenylacetic acid to dioxindole with zinc dust and sulphuric acid, mentions that he obtained as by-product, *o*-azophenylacetic acid. On reducing *o*-nitro-*p*-methoxyphenylacetic acid under the same conditions, the main product isolated was the azoxy-derivative. *o*-Nitro-*p*-methoxyphenylpyruvic acid (1·7 grams) was oxidised with hydrogen peroxide to *o*-nitro-*p*-methoxyphenylacetic acid under the conditions given in the last section, and the latter acid was precipitated by adding sulphuric acid (10 c.c. of 50 per cent.). Zinc dust (1·3 grams of 90 per cent.) was then added in small quantities and with vigorous shaking, the temperature being kept at about 30°. After remaining over-night, the solid was collected, washed well, and recrystallised from 50 per cent. acetic acid, from which the azoxy-derivative separated in stout, brownish-yellow needles which melted at 173—174° (Found: C = 58·0; H = 5·1; N = 8·0. $C_{18}H_{18}O_7N_2$ requires C = 57·7; H = 4·8; N = 7·5 per cent.).

6-*Methoxyindole-2-carboxylic Acid* (Formula XXXVI).

This acid is obtained from *o*-nitro-*p*-methoxyphenylpyruvic acid by reduction with ferrous sulphate and ammonia under the conditions already described in detail in the case of the preparation of indole-2-carboxylic acid from *o*-nitrophenylpyruvic acid (p. 1625). The only point of difference is that the ammonium salt of the methoxy-acid is less soluble than that of the unsubstituted acid, and usually crystallises out to some extent from the filtrate of the ferric oxide sludge, which requires therefore to be well washed with hot water. On acidifying the ammoniacal filtrate, 6-methoxyindole-2-carboxylic acid separates as a sandy, crystalline powder, the yield being about 70 per cent. calculated on the pyruvic acid employed (Found: $C = 63{\cdot}0$; $H = 4{\cdot}7$. $C_{10}H_9O_3N$ requires $C = 62{\cdot}8$; $H = 4{\cdot}7$ per cent.).

6-*Methoxyindole-2-carboxylic acid* closely resembles indole-2-carboxylic acid in appearance and in many of its properties. It melts at 196—197°, and decomposes a few degrees above this into carbon dioxide and 6-methoxyindole (see below). It is readily soluble in boiling alcohol, and, when the solution is allowed to cool slowly, the acid separates in well-defined, prismatic needles. It crystallises from acetic acid in lustrous plates which lose their lustre on heating in the water-oven owing to elimination of acetic acid of crystallisation. The boiling solution in alcoholic hydrochloric acid gives with *p*-dimethylaminobenzaldehyde, a red coloration, which almost disappears on cooling; the addition of sodium nitrite then produces a deep greenish-blue coloration.

6-*Methoxyindole* (Formula XXXIX).

This new derivative of indole is obtained when 6-methoxyindole-2-carboxylic acid is cautiously heated in a test-tube by means of a sulphuric acid bath somewhat above its melting point (197°) until decomposition is complete. The residue is boiled with water containing a little sodium carbonate and filtered hot, when, on cooling, 6-methoxyindole separates in colourless, glistening leaflets (Found: $C = 73{\cdot}2$; $H = 6{\cdot}2$. C_9H_9ON requires $C = 73{\cdot}4$; $H = 6{\cdot}1$ per cent.).

6-*Methoxyindole* melts at 91—92° and has a faint and not unpleasant odour somewhat reminiscent of that of indole, with which substance it exhibits considerable similarity in appearance and properties.

It is readily soluble in the usual organic solvents with the exception of light petroleum, from which it can very conveniently be recrystallised. When heated in alcoholic solution with *p*-dimethylaminobenzaldehyde and a drop of hydrochloric acid, a purplish-red colour develops, which does not fade on cooling. The addition of a drop of sodium nitrite intensifies the colour. If, however, the alcoholic solution is mixed with several drops of hydrochloric acid and heated, the initially red solution becomes more deeply coloured, then bluer, and ultimately a somewhat faint greenish-blue, and the colour is intensified by adding nitrite.

6-*Methoxyindole*-2-*carboxyacetalylamide* (Formula XL).

This substance is obtained by the action of aminoacetal on the chloride of 6-methoxyindole-2-carboxylic acid essentially under the conditions described in detail in the case of the preparation of indole-2-carboxyacetalylamide (p. 1626). The principal difference noticed was that the methoxy-acid appeared to react more readily and smoothly with phosphorus pentachloride than the unsubstituted acid (Found: C = 62·9; H = 7·2. $C_{16}H_{22}O_4N_2$ requires C = 62·7; H = 7·2 per cent.).

This acetalylamide is very similar in appearance and properties to indole-2-carboxyacetalylamide, and is also decomposed on heating with elimination of alcohol and formation of a resinous substance.

It melts at 123° and crystallises well from benzene, in which solvent, as also in alcohol, it is more readily soluble than the simpler compound.

11-*Methoxy*-5-*keto*-4 : 5-*dihydroindolediazine* (1 : 4) (Formula XLI).

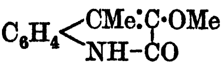
In preparing this substance, 6-methoxyindole-2-carboxyacetalylamide is added to a saturated solution of hydrogen chloride in alcohol and kept at 40—45° until yellow crystals separate. After remaining over-night, the precipitate is collected and recrystallised from alcohol (Found: C = 67·1; H = 4·8. $C_{12}H_{10}O_2N_2$ requires C = 67·3; H = 4·7 per cent.).

Methoxyketodihydroindolediazine melts at 253° with previous sintering. It is moderately soluble in acetone, less soluble in alcohol, and still less so in benzene, and separates from alcohol in well-defined, yellow needles. Both this substance and ketodihydroindolediazine (m. p. 247°; p. 1627) exhibit a vivid blue fluorescence in neutral or alkaline, but not in acid, solution, and this effect is best seen with the aid of the light of burning magnesium ribbon.

3-*Methylindole-2-carboxylic Acid* (*Scatole-2-carboxylic Acid*) (Formula XXV).

It is stated in the introduction (p. 1609) that this acid may be conveniently prepared from the product of the condensation of *o*-nitrotoluene with ethyl oxalate and sodium ethoxide, by direct methylation followed by the reduction of the product. The condensation product prepared as recommended by Reissert (*Ber.*, 1897, **30**, 1030), after keeping at 40° for three days, is cooled and the red, gelatinous mass mixed with one and a half times the calculated quantity of methyl iodide, when decomposition sets in at once with some evolution of heat. The mixture is heated to boiling for two days, during which the red colour changes to brown, the alcohol and excess of methyl iodide are then distilled off under reduced pressure, water is added, and the whole extracted three times with ether. After washing well with water and drying over calcium chloride, the ethereal solution is allowed to remain over-night, during which it deposits a small quantity of a reddish-brown, crystalline substance, which was not further examined. The filtered ethereal solution is evaporated and the yellowish-brown syrup—which presumably consists mainly of *ethyl* α-*keto*-β-o-*nitrophenylbutyrate*, $C_6H_4(NO_2)\cdot CHMe\cdot CO\cdot CO_2Et$—(5 grams) is dissolved in glacial acetic acid (30 c.c.) and gradually reduced by zinc dust (13 grams of 90 per cent.), the addition of the latter being so regulated that the temperature does not rise above 50°. The product is mixed with water, extracted several times with ether, the ethereal solution, which exhibits a striking bluish-green fluorescence, washed with water and dilute sodium carbonate solution, and quickly dried over potassium carbonate, during which 3-*methoxy*-4-*methyl*-α-*quinolone* commences to separate (see below). The ethereal solution is rapidly filtered and left for two days in the ice chest, filtered from the quinolone and evaporated, when a yellow syrup remains which gradually crystallises and ultimately becomes semi-solid. Purification is best achieved by distilling the whole under reduced pressure, when the ethyl ester passes over at 210°/8 mm., leaving a considerable carbonaceous residue. The ester soon solidifies, and may be crystallised from alcohol, from which it separates in stout needles melting at 135° (compare Wislicenus and Arnold, *Annalen*, 1888, **246**, 334) (Found: $C = 70{\cdot}7$; $H = 6{\cdot}4$. $C_{12}H_{13}O_2N$ requires $C = 70{\cdot}9$; $H = 6{\cdot}4$ per cent.).

3-*Methylindole-2-carboxylic acid* is readily obtained from the ester by boiling with methyl-alcoholic potassium hydroxide, adding water, evaporating off the methyl alcohol, and acidifying with hydrochloric acid, when the acid separates as a putty-like mass, which soon solidifies and crystallises well from dilute acetic acid in needles melting at 164° (Found: C = 68·5; H = 5·2. $C_{10}H_9O_2N$ requires C = 68·6; H = 5·1 per cent.).

3-*Methoxy-4-methyl-α-quinolone*,  $C_6H_4<\begin{matrix}CMe{:}C{\cdot}OMe \\ NH-CO\end{matrix}$ (cf. p. 1610).

This substance, obtained as described above, is produced only in a yield of about 2 per cent. under these conditions. It melts at 217°, is almost insoluble in ether, and sparingly so in alcohol, from which it separates in concentric groups of needles (Found: C = 70·0; H = 5·6; N = 7·4; MeO = 16·9. $C_{11}H_{11}O_2N$ requires C = 69·8; H = 5·8; N = 7·4; MeO = 16·4 per cent.). Methoxymethylquinolone is insoluble in warm dilute ammonia, but dissolves immediately in methyl-alcoholic potassium hydroxide (25 per cent.) in the cold, and a crystalline substance is deposited, which is apparently a potassium derivative. On acidifying with hydrochloric acid, the quinolone separates as a chalky mass consisting of microscopic, fern-like leaves.

3-*Methylindole-2-carboxyacetalylamide* (Formula XXX).

In preparing this substance, 3-methylindole-2-carboxylic acid (1·7 grams) was suspended in freshly distilled acetyl chloride (20 grams) and gradually mixed with phosphorus pentachloride (2·1 grams), rise of temperature being avoided. The product was treated exactly as described in the case of the chloride of indole-2-carboxylic acid (p. 1626) and very carefully mixed with a dry chloroform solution of aminoacetal (3 grams), and it is necessary in this case to take special care to avoid rise of temperature, otherwise a dark product is obtained.

After distilling off the chloroform under reduced pressure, the residue is recrystallised from benzene. The yield is more than 80 per cent. of theory (Found: C = 66·4; H = 7·7. $C_{16}H_{22}O_3N_2$ requires C = 66·2; H = 7·6 per cent.).

3-*Methylindole-2-carboxyacetalylamide* separates from benzene, in which it is moderately readily soluble, in colourless needles and melts at 115°.

5-*Keto-7-methyl-4 : 5-dihydroindolediazine* (1 : 4) (Formula XXXI).

This substance is obtained when 3-methylindole-2-carboxyacetalylamide is mixed with alcoholic hydrogen chloride and the mixture warmed to 40—45° (compare p. 1627). Yellow crystals separate, which are collected and twice recrystallised from alcohol (Found: $C = 72{\cdot}9$; $H = 5{\cdot}0$. $C_{12}H_{10}ON_2$ requires $C = 72{\cdot}7$; $H = 5{\cdot}0$ per cent.).

This substance melts at 210° and in appearance and properties closely resembles 5-keto-4 : 5-dihydroindolediazine (p. 1627). Both substances dissolve in alcohol, yielding pale yellow solutions which fluoresce green. When sodium is added to the solution of either in boiling butyl alcohol, reduction takes place and the solutions exhibit a remarkable yellowish-green fluorescence. Again, both substances couple readily with diazotised sulphanilic acid, yielding dyes which dissolve in alkalis with an orange-yellow and in acids with a yellow colour and dye wool yellow from an acid bath. The relation of these substances to 1-methyl*iso*quinolone is a close one both in regard to formal constitution and properties.

1 : 3-*Dimethylindole-2-carboxylic Acid* (Formula XXXII).

This acid, which does not appear to have been previously described, is obtained from α-ketobutyric acid by simply heating with *as.*-phenylmethylhydrazine and hydrochloric acid on the steam-bath. Methyloxalacetic ester (Wislicenus and Arnold, *Annalen*, 1888, **246**, 336; 12 grams) is added to a mixture of concentrated hydrochloric acid (30 c.c.) and water (60 c.c.) and the whole gently boiled until the evolution of carbon dioxide has ceased and the oil has completely disappeared. After allowing to cool, crude phenylmethylhydrazine * (10 grams) is added and the mixture heated on the steam-bath, when, in a short time, needles of dimethylindolecarboxylic acid commence to separate and soon fill the liquid. The acid, after being collected, washed, and dried at 100°, melts at 197—200° and the yield is almost theoretical. In this condition it may be used directly for the work described below. For analysis, it was recrystallised from benzene containing a little alcohol (Found: $C = 70{\cdot}0$; $H = 6{\cdot}0$; $N = 7{\cdot}6$. $C_{11}H_{11}O_2N$ requires $C = 69{\cdot}9$; $H = 5{\cdot}8$; $N = 7{\cdot}4$ per cent.).

1 : 3-*Dimethylindole-2-carboxylic acid* decomposes suddenly at about 213° without previous fusion. It is readily soluble in alcohol, but almost insoluble in cold benzene or light petroleum, and separates from a mixture of benzene and alcohol as a colourless crystalline powder. The alcoholic solution, mixed with *p*-dimethylaminobenzaldehyde and hydrochloric acid, gives no coloration until nitrite is added and then a red colour develops, which slowly fades.

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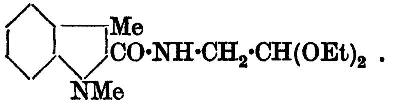
* For such purposes, the crude mixture of phenylmethylhydrazine with some methylaniline which results from the reduction of nitrosomethylaniline with zinc dust and acetic acid may be generally used with success.

1 : 3-*Dimethylindole-2-carboxyacetalylamide*,



In preparing this substance, 1 : 3-dimethylindole-2-carboxylic acid is first made into the acid chloride with acetyl chloride and phosphorus pentachloride in the usual manner (p. 1626), and this is then condensed with aminoacetal in chloroform solution. After distilling off the chloroform and adding water, the crystalline mass is collected, dried on porous porcelain, and crystallised from a mixture of benzene and light petroleum (Found: $C = 67{\cdot}1$; $H = 7{\cdot}9$. $C_{17}H_{24}O_3N_2$ requires $C = 67{\cdot}2$; $H = 7{\cdot}9$ per cent.).

This substance separates from a mixture of benzene and light petroleum in long, colourless hairs and melts at 110—111°. In its properties, and especially in its manner of crystallising from various solvents, it differs rather markedly from the other substituted aminoacetals described in this communication. Although there was no probability of a diazine being formed, some of the substance was treated in the usual manner with alcoholic hydrogen chloride (p. 1627), but no darkening of the solution took place, nor did crystals separate. On adding water, a sticky substance was deposited, which may have been the corresponding aldehyde, or an oxazole derivative, but the matter was not further investigated.

1-*Methylindole-2-carboxyacetalylamide* (Formula XXXIII).

The 1-methylindole-2-carboxylic acid required for the preparation of the above substance was obtained from phenylmethylhydrazine and pyruvic acid by the method described by E. Fischer and O. Hess (*Ber.*, 1884, **17**, 561). This acid gives, in alcoholic solution, with *p*-dimethylaminobenzaldehyde and hydrochloric acid, a deep purple coloration which fades somewhat on cooling. A drop of sodium nitrite then gives a more intense red, which fades on boiling.

The acid chloride was made by acting on the acid (3·5 grams) with acetyl chloride (30 c.c.) and phosphorus pentachloride (4·2 grams) in the usual manner (p. 1626). The conversion of the chloride into 1-methylindolyl-2-aminoacetal also proceeds normally (p. 1626), but the product, after distilling off the chloroform, exhibited little tendency to crystallise until it was rubbed with water. The crude crystalline mass, after being collected and dried, weighed 4·6 grams and was nearly pure (m. p. 102—103°). For analysis, it was recrystallised from benzene and then melted at

106—107° (Found: C = 66·4; H = 7·6. $C_{16}H_{22}O_3N_2$ requires C = 66·2; H = 7·6 per cent.).

2-*Keto*-1-*methyl*-2 : 3-*dihydro*-4-*carboline* (*Ketomethyldihydronorharman*) (Formula XXXIV).

This interesting substance is obtained when 1-methylindole-2-carboxyacetalylamide is warmed with alcoholic hydrogen chloride at 40—45° for a few minutes. The colourless crystals which separate are collected and appear to consist of a hydrochloride, and this must not be washed with alcohol, since it is soluble in alcohol containing hydrogen chloride. If, however, the substance, after draining on porous porcelain, is dissolved in much hot alcohol, ketomethyldihydrocarboline itself separates, on cooling, in long, colourless needles. For analysis, the substance was again crystallised from alcohol (Found: C = 72·7; H = 5·0. $C_{12}H_{10}ON_2$ requires C = 72·7; H = 5·0 per cent.).

2-*Keto*-1-*methyl*-2 : 3-*dihydro*-4-*carboline* melts at 242° and is generally more readily soluble in organic solvents than 5-keto-4 : 5-dihydroindolediazine (m. p. 247°; p. 1627). Unlike the latter substance, it is appreciably soluble in boiling water. Its basic character is definite although feeble, and it is also phenolic. In both acid and alkaline solution it exhibits blue fluorescence.

Synthesis of 4-*Carboline* (*Norharman*) (Formula II).

2-Keto-1-methyl-2 : 3-dihydro-4-carboline, finely powdered and intimately mixed with twenty times its weight of pure zinc dust, was cautiously distilled in a stream of hydrogen over a layer of zinc dust about eighteen inches long contained in a hard-glass tube heated in a combustion furnace. The distillate was a pale yellow resin and the portion of the tube containing it was cut out, ground, and extracted with boiling dilute acetic acid with the addition of a little animal charcoal. The filtered solution exhibited intense blue fluorescence, and on the addition of a hot solution of picric acid gave a voluminous precipitate of a picrate. This was collected and recrystallised twice from hot water. The base was then regenerated into ether by means of dilute potassium hydroxide and the ethereal solution well washed with concentrated aqueous potassium hydroxide and dried over the solid reagent. The residue, after removal of the solvent, could be crystallised from benzene and had all the properties of norharman. The melting point was always unsatisfactory, however, and as it seemed probable that this was due to admixture of norharman with its *N*-methyl derivative, the following procedure was adopted. The base was dissolved in dilute hydrochloric acid, the benzene mother-liquors and the apparatus employed in crystallisations were washed with the same reagent, and the combined solutions were concentrated, and the base precipitated by the addition of ammonia, collected, washed with water, and dried in air. The material was then mixed with a little hydriodic acid (*d* 1·8) and heated in a test-tube in a sulphuric acid bath to about 300°. The process was repeated twice and the product triturated with sulphurous acid, dissolved in hot alcohol, and after the addition of potassium hydroxide diluted with water and extracted with ether. The ethereal solution was washed with aqueous potassium hydroxide and then with water and finally with dilute nitric acid. This acid extract was concentrated on the steam-bath and on cooling the nitrate crystallised in pale yellow needles. The salt was once recrystallised from hot dilute nitric acid and the base was then regenerated and crystallised from benzene. The compound was thus obtained in colourless needles melting at 198° and at the same temperature when mixed with a specimen of norharman obtained as described on p. 1619.

6-*Methoxy*-3-*methylindole*-2-*carboxylic Acid* (Formula XLIII).

This acid was synthesised from *o*-nitro-*p*-tolyl methyl ether (p. 1629) in a manner similar to that employed in the synthesis of 3-methylindole-2-carboxylic acid from *o*-nitrotoluene (p. 1634). Sodium (4·6 grams), dissolved in alcohol (70 c.c.), was cooled, mixed with ethyl oxalate (14·6 grams) and then *o*-nitro-*p*-tolyl methyl ether (8·3 grams) added. After keeping for three days at 40°, the thick, dark red mass was thoroughly mixed with methyl iodide (28 grams) and the whole heated under reflux for twenty-four hours, when the red colour had almost disappeared.

The alcohol and excess of methyl iodide were distilled off under reduced pressure, water was added, and the mass extracted several times with ether. The ethereal extract was washed with water, dried over calcium chloride, and the ether distilled off, when a syrup remained which did not crystallise but evidently consisted of *ethyl* α-*keto*-β-o-*nitro*-p-*methoxyphenylbutyrate*, $MeO\cdot C_6H_3(NO_2)\cdot CHMe\cdot CO\cdot CO_2Et$. The syrup was dissolved in glacial acetic acid (200 c.c.), and zinc dust (30 grams of 90 per cent.) added with constant shaking at such a rate that the acetic acid almost boiled. When all had been added, the whole was boiled for a few minutes, filtered with the aid of the pump, and water added to the filtrate, when an oil separated, which rapidly solidified, and more was obtained by extracting the zinc precipitate and solution with ether. After draining on porous porcelain, the solid was recrystallised from a little alcohol, when colourless crystals were obtained which melted at 128° and consisted of *ethyl* 6-*methoxy*-3-*methylindole*-2-*carboxylate*.

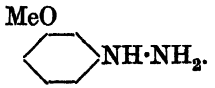
This ester is readily soluble in alcohol, sparingly so in benzene, and almost insoluble in light petroleum (Found: C = 67·1; H = 6·3. $C_{13}H_{15}O_3N$ requires C = 67·0; H = 6·4 per cent.).

This ester was hydrolysed by boiling with methyl-alcoholic potassium hydroxide, water was added, the solution evaporated until free from methyl alcohol and acidified with hydrochloric acid, when 6-*methoxy*-3-*methylindole*-2-*carboxylic acid* separated as a colourless, crystalline powder, which melted at 200—202° without decomposition and in appearance and many of its properties resembled 3-methylindole-2-carboxylic acid (m. p. 164°; p. 1634).

6-*Methoxy*-3-*methylindole* (6-*Methoxyscatole*) (Formula XLIV).

In order to prepare this substance, 6-methoxy-3-methylindole-2-carboxylic acid contained in a narrow test-tube was heated to about 210° by means of a sulphuric acid bath, when it effervesced and a white sublimate of lustrous plates condensed on the sides of the tube. A further quantity was obtained by extracting the rather tarry residue in the tube with boiling, very dilute sodium carbonate solution, the filtered solution, on standing, depositing almost colourless leaflets. The crystalline sublimate melted directly at 125° and consisted of 6-*methoxy*-3-*methylindole*, since a mixed melting point showed that it was identical with the substance obtained by the action of heat on 6-methoxy-2-carboxyindole-3-acetic acid (p. 1641). 6-*Methoxy*-3-*methylindole* has a faint and not unpleasant odour, and is very readily soluble in the usual organic solvents. A splinter of a crystal dissolved in alcohol and mixed with *p*-dimethylaminobenzaldehyde and a drop of hydrochloric acid develops a bluish-green colour, which becomes yellowish-green on the addition of more hydrochloric acid. On warming the solution, a rich bluish-purple colour develops, which is changed to deep bluish-violet by a drop of sodium nitrite. A pine shaving moistened with hydrochloric acid is coloured bluish-violet by this substituted indole.

m-*Methoxyphenylhydrazine*,



This substance, which had not previously been obtained, was required for the synthesis of the acid described in the next section, and was prepared from *m*-anisidine by the following process: *m*-Anisidine (61·5 grams) is added to hydrochloric acid (500 c.c. of *d* 1·16), cooled in a freezing mixture and the whole vigorously stirred, when the hydrochloride of the base separates as a thick paste.

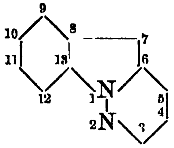
Sodium nitrite (150 c.c. containing 0·23 gram per c.c.) is gradually added, the stirring being continued and the whole kept at 0°. A well-cooled solution of stannous chloride (350 grams) in hydrochloric acid (300 c.c.) is run in slowly and after about four hours the heavy, white precipitate is collected, well pressed, and shaken with sodium hydroxide solution (400 c.c. of 25 per cent.) and ether (250 c.c.) and the ethereal layer separated. The aqueous solution is extracted twice more with ether, the combined ethereal extracts are dried over potassium carbonate, the ether is distilled off, and the residual oil fractionated under reduced pressure, when m-*methoxyphenylhydrazine* passes over at 166—168°/15 mm. as a colourless oil. On standing in a freezing mixture, this solidifies to a mass of colourless needles, which melt again at room temperature (Found: N = 20·1. $C_7H_{10}ON_2$ requires N = 20·3 per cent.).

6-*Methoxy*-2-*carboxyindole*-3-*acetic Acid* (Formula XLVI).

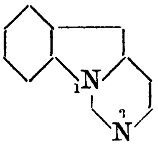
As stated in the introduction (p. 1614), this acid is formed when the condensation product of α-ketoglutaric acid and *m*-methoxyphenylhydrazine is treated with alcoholic hydrogen chloride. *m*-Methoxyphenylhydrazine (4 grams) is dissolved in alcohol (25 c.c.), α-ketoglutaric acid (4 grams) added, and then gaseous hydrogen chloride passed sufficiently rapidly to raise the alcohol nearly to the boiling point. The liquid becomes brown and then green, ammonium chloride separates, and after two hours the latter is filtered off and most of the alcohol distilled from the filtrate under reduced pressure. On diluting with water, a sticky ester separates, and this is hydrolysed by boiling with methyl-alcoholic potassium hydroxide, water is added, the methyl alcohol removed by distillation under reduced pressure, and the residue acidified, when a sticky mass separates, which is rapidly removed by filtration. On standing, the solution deposits needles which, after recrystallisation from dilute acetic acid, melt at 224—225°. This acid was not analysed owing to the very small yield, but it is evidently 6-*methoxy*-2-*carboxyindole*-3-*acetic acid*, because, when heated, it decomposed with evolution of carbon dioxide and formation of 6-methoxy-3-methylindole (6-methoxyscatole), which melted at 125° and was identical with the substance obtained from 6-methoxy-3-methylindole-2-carboxylic acid by the action of heat (p. 1640).

Note on Nomenclature.

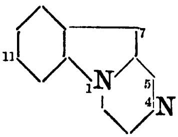
There are four theoretically possible heterocyclic types containing fused indole and diazine nuclei, and these isomerides of the carbolines, naphthiminazoles, etc., are figured below. It is suggested that the name "indolediazine" is the most rational description possible, and the system of numbering is similar to that already adopted in the case of the carbolines (compare T., 1919, **115**, 970).



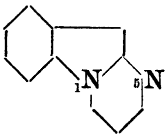
Indolediazine (1 : 2).



Indolediazine (1 : 3).

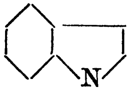


Indolediazine (1 : 4).



Indolediazine (1 : 5).

It should be noted that the numbering is counter-clockwise because the indole nucleus is written



In Richter's "Lexicon" the numbering is usually clockwise, but the result is identical because the indole nucleus is inverted.

We desire to thank Dr. J. Kenyon and Captain J. R. H. Whiston, M.A., for assistance in the preparation of α-ketoglutaric acid, *o*-nitro-*p*-tolyl methyl ether, and certain other substances required in considerable amount in the course of this investigation. Our thanks are also due to Mr. F. Hall, who carried out a large proportion of the necessary analyses.

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[*Received, August* 10*th*, 1921.]

CLXXXVI.—*The Molecular Conductivity of some Sulphonium Compounds in Acetone.*

By Sir Praphulla Chandra Rây and Kalikumar Kumar.

In recent years one of the authors has prepared a large number of new sulphonium compounds which are insoluble in water but are generally soluble in acetone. The acetone solutions of these compounds are fairly good conductors, indicating that the substances behave as salts. An investigation of the conductivity of these compounds was therefore undertaken, with results which are tabulated below. The molecular conductivity increases regularly with dilution and its magnitude is similar to that observed for potassium iodide. These compounds appear, therefore, to be true salts having molecular weights represented by their respective chemical formulæ, and dissociating as uni-univalent electrolytes, possibly into a negative iodine ion and a complex positive ion containing the sulphur chain.

The sulphonium compounds used in the present investigation have already been described (T., 1916, **109**, 1, 135, 606; 1919, **115**, 551, 1152).

Merck's chemically pure acetone was used. It was further purified by rectification over anhydrous calcium chloride, and had the constant b. p. 55·8°; its specific conductivity was $3{\cdot}3 \times 10^{-6}$ reciprocal ohms at 27°. The temperatures of the different experiments were between 26·8° and 28·8°, and the results are expressed for the temperature 27·8°.

The results obtained in the conductivity experiments are tabulated below, where V is the volume in litres containing a gram-molecular weight of the salt.

Conductivity of Sulphonium Compounds in Acetone Solution at 27·8°.

Compound.	$V = 64$.	$V = 128$.	$V = 256$.	Remarks.
(1) $EtMeS_2,MeI,2HgI_2$	—	168·1	181·9	One hexad and one tetrad sulphur atom.
(2) $Et_2S_2,EtI,2HgI_2$	114·5	135·4	144·3	
(3) Et_2S,MeI,HgI_2	124·2	133·6	142·4	One hexad sulphur atom.
(4) Et_2S,EtI,HgI_2	—	125·1	139·4	
(5) Et_2S,PrI,HgI_2	113·3	121·7	136·9	
(6) Et_2S,BuI,HgI_2	113·0 *	120·5	132·3	* At $V = 63{\cdot}8$.
(7) Me_2S_2,MeI,HgI_2	—	140·4	149·0	Chain compound with two tetrad sulphur atoms.
(8) Me_2S_2,EtI,HgI_2	126·9	140·3	—	
(9) $MeEtS_2,EtI,HgI_2$	127·0	139·0	—	
(10) Et_2S_2,EtI,HgI_2	119·7	132·4	142·8	
(11) Pr_2S_2,MeI,HgI_2	117·6	129·3	140·3	
(12) Et_2S_2,PrI,HgI_2	112·2	125·3	133·6	
Potassium Iodide	—	115·5	130·5	At 25°

Discussion.

The disulphonium chain compounds with one hexad and one tetrad sulphur atom give the best conducting solutions in acetone. They are followed by the monosulphonium hexad compounds, whilst the disulphonium compounds with two tetrad sulphur atoms give the smallest conductivities, comparable with the values for potassium iodide in acetone solution.

The conductivities of similar compounds diminish, without exception, with increasing molecular weight, for example, on comparing the compounds numbered (1) and (2) it will be found that the replacement of two methyl groups by two ethyl groups lowers the conductivity from 168·1 to 135·4. This relation between conductivity and molecular weight is borne out by the values for the compounds (3), (4), and (5), and those for the compounds (9), (10), and (11).

The compounds (11) and (12) have identical molecular weights, but show an appreciable difference in their conducting power. This is probably due to the relative difference in the magnitude of the aliphatic radicles of the two compounds. Thus the methyl and propyl radicles differ by two methylene groups, whereas ethyl and propyl differ by only one.

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[*Received, June 28th*, 1921.]

CLXXXVII.—*The Essential Oil from* Andropogon iwarancusa, *Jones, and the Constitution of Piperitone.*

BY JOHN LIONEL SIMONSEN.

FOR some time past the author has been investigating the oil obtained by the distillation of the grass—*Andropogon iwarancusa*, Jones.* As the main constituent of the oil (approximately 80 per cent.) was found to be a ketone identical apparently with piperitone, it appears desirable, in view of the recent publication of the paper by Smith and Read (this vol., p. 779) dealing with the properties of piperitone, to place on record the results so far obtained, leaving to these authors the further investigation of this interesting ketone.

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* Mr. R. S. Hole, Forest Botanist, has kindly furnished me with the following botanical note :

Taxonomy.

In 1889, Hackel described the following forms :

(1) *Andropogon laniger*, Desf., var. *α genuinus* from Africa, Arabia, and India, var. *β grandiflorus* from Persia.

(2) *Andropogon iwarancusa*, Blanc, var. *α genuinus* from India, var.

Andropogon iwarancusa, Jones, occurs in the Himalayas and outer hill zone from Kashmir to Assam ascending to 8000 ft. and above; in the plains from North West Himalaya to Bombay Presidency.

The oil from *A. iwarancusa*, Jones, does not appear to have been previously investigated, although the constituents of the oil of the closely related grass, *Cymbopogon sennaarensis*, Chiov., have been examined by Roberts (T., 1915, **107**, 1465). The oil used in this research was kindly placed at the disposal of the author by Colonel Johnson of Abbotabad, and had been obtained in a yield of about 1 per cent. by steam distillation in the usual manner. It has been found to be of comparatively simple composition, consisting of a terpene, which has not up to the present been identified and is being further investigated, together with a ketone which has properties agreeing in nearly all respects with those of *dl*-piperitone isolated by Read and Smith from *Eucalyptus dives* except that it was found to be strongly dextrorotatory ($[\alpha]_D^{30^\circ}$ + 36·76°). The properties of this ketone would further appear to be identical with those of the ketones isolated by Schimmel & Co. (Report 1910, p. 97) from

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β *sennaarensis* from Africa, var. γ *proximus* from Africa (DC. *Mon. Phan.*, Vol. VI, pp. 598—601).

In 1906, Dr. Stapf pointed out that the correct, original name of (2) was *Andropogon iwarancusa*, Jones (*Kew Bull.*, 1906, p. 314); at the same time he suggested breaking up the large genus *Andropogon* as understood by Hackel, and the definition of Hackel's two Indian plants as distinct species under the names of (1) *Cymbopogon schœnanthus*, Spreng, and (2) *Cymbopogon iwarancusa*, Schult (*loc. cit.*, pp. 352—354). Dr. Stapf, however, remarks that "It is not impossible that the distinguishing characters of *C. iwarancusa* as compared with *C. schœnanthus*, namely, the robust state, the long, flat, and relatively broad leaves, and the more composite panicles, are mainly due to edaphic influences," and when speaking of the distribution of *C. schœnanthus* says "the eastern limit is ill-defined, as here the areas of *C. schœnanthus* and *C. iwarancusa* overlap, and numerous transition forms occur" (*loc. cit.*, pp. 314, 353). These plants are now being studied at the Forest Research Institute, Dehra Dun, with the object of deciding what forms, if any, are really distinct and can be distinguished by well-marked and constant characters, morphological or chemical, and meanwhile it is believed to be advisable to follow the *Flora of British India*, VII, p. 203, and to deal with the Indian forms of this plant as a single species under the name *Andropogon iwarancusa*, Jones.

Japanese peppermint oil and by Roberts (*loc. cit.*) from *C. sennaarensis*. These authors considered the ketones isolated by them to be identical with Δ^1-*p*-menthen-3-one, which had been prepared synthetically by Wallach (*Annalen*, 1908, **362**, 272) from 1 : 3 : 4-trihydroxyterpane. This view of the constitution was based (*a*) on the identity of the properties of the derivatives (semicarbazones and oximes) and (*b*) on the products of oxidation, namely, thymol, diosphenol, α-hydroxy-α-methyl-δ-*iso*propyladipic acid, γ-acetyl-α-*iso*propylbutyric acid, and α-*iso*propylglutaric acid. The isolation of these products would appear to leave little doubt that these ketones had the constitution assigned to them unless some molecular rearrangement had taken place during the oxidation.

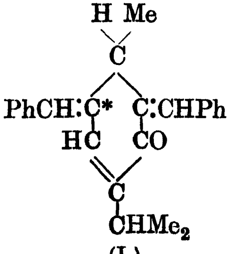
Read and Smith (*loc. cit.*) would appear to consider *dl*-piperitone to be not identical with Δ^1-*p*-menthen-3-one, although they point out that it must be a *p*-menthenone, since menthol was formed on reduction and thymol on oxidation with ferric chloride. Although they expressly leave the discussion of the constitution of *dl*-piperitone to a future communication (*loc. cit.*, p. 783), they apparently base their present view that it cannot be identical with any known *p*-menthenone mainly on the fact that on treatment with benzaldehyde in the presence of alkali a benzylidene derivative was formed. They have also recorded melting points for the semicarbazone, oxime, and hydroxylamino-oxime differing somewhat from those given to the similar derivatives of Δ^1-*p*-menthen-3-one.

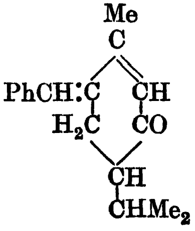
The ketone obtained by the author, apart from its optical activity, had constants agreeing fairly well with those found for *dl*-piperitone and also with those recorded by Wallach (*loc. cit.*) for Δ^1-*p*-menthen-3-one. When purified through its sodium sulphite compound, the ketone was almost completely racemised ($[\alpha]_D^{20}$ + 7·92°), a fact readily explicable if it is assumed that in the presence of alkali enol formation takes place with consequent loss of the asymmetric carbon atom. This view is supported by the fact that the ketone is also racemised by treatment with dilute alkali and all derivatives prepared in the presence of alkali were found to be optically inactive. The identity of the racemic ketone with *dl*-piperitone would appear to be definitely proved (*a*) by the formation of a benzylidene derivative, m. p. 61°, and a hydroxylamino-oxime, m. p. 170—171°, (*b*) by oxidation to thymol with ferric chloride, and (*c*) by reduction to menthol. On the other hand, a slight divergence from the results obtained by Read and Smith was observed in the melting points of the semicarbazone and oxime. When the ketone was treated with semicarbazide hydrochloride in the usual manner, a mixture of two semicarbazones was obtained; the α-semicarbazone melted at 225—227° and the β-semicarbazone at 174—176° (Schimmel and Co., *loc. cit.*, give 224—225° and 170—171° as the melting points of these two semicarbazones). For the oxime also a somewhat higher melting point has been obtained by the author, namely, 117—118° (Read and Smith give 110—111°). The author would suggest that the somewhat lower melting point for the semicarbazone observed by Read and Smith was due to its not having been quite free from the more fusible isomeride, which the author has found to be removed only with considerable difficulty on crystallisation from alcohol, the solvent used by these authors. By the use of acetic acid, the α-semicarbazone was obtained pure after two crystallisations. The considerably higher melting point obtained in the case of the oxime is somewhat more difficult to understand, but it is possible that Read and Smith's specimen was contaminated with a trace of the stereoisomeride. Some support is lent to this suggestion in that the author, on one occasion, on boiling the pure oxime (m. p. 117—118°) with an excess of hydroxylamine hydrochloride and sodium acetate for some days with the object of preparing the hydroxylamino-oxime, obtained as the product an oxime which was obviously a mixture and melted indefinitely at 90°; analysis established the absence of any impurity and on fractional crystallisation a small quantity of the pure oxime of m. p. 117—118° was separated, but it was not found possible to isolate the stereoisomeride, which was undoubtedly present, in a pure state. On warming the mixture of oximes for some time with a little dilute alkali, the whole was reconverted into the oxime of m. p. 117—118°.

When the active ketone was treated with semicarbazide hydrochloride, in addition to the inactive α-semicarbazone of m. p. 225—227°, an active β-*semicarbazone* melting at 193—194° was obtained. As was to be expected in a substance possessing a system of conjugate linkings, the rotatory power was considerably higher than that of the ketone from which it was derived, the rotation at the same time having become negative. Attempts to prepare an optically active oxime were unsuccessful; the active ketone, on treatment with hydroxylamine hydrochloride in the manner found suitable for the preparation of the inactive oxime, yielded an oil from which a small quantity of the inactive oxime could be isolated, whilst if dilute alkali was used in place of sodium acetate to neutralise the hydrochloric acid the inactive oxime was obtained in an excellent yield. An optically active *hydroxylamino-oxime acetate* was, however, prepared (see p. 1652).

Reference has already been made to the fact that Schimmel & Co. and Roberts (*loc. cit.*) obtained on oxidation a variety of products which left no doubt as to the constitution of the ketones investigated by them. When the ketone from *A. iwarancusa* oil was oxidised in ice-cold alkaline solution with potassium permanganate, the main product of the reaction was *l*-γ-acetyl-α-*iso*propylbutyric acid. This acid, which was obtained as an oil, was identified by conversion into its semicarbazone, which melted, as stated by Wallach (*Annalen*, 1910, **379**, 188), at 150—152°. On oxidation of the oily acid with hypobromite solution in the usual manner, a quantitative yield of *dl*-α-*iso*propylglutaric acid melting at 94—95° was obtained, and this acid showed all the properties assigned to it by Perkin (T., 1896, **69**, 1495).

In the author's opinion, the identity of the ketone obtained from *A. iwarancusa* oil with piperitone cannot be doubted, and it must be regarded as d-*piperitone.* Further, from a consideration of the products formed on oxidation, there can be no doubt that this ketone is *d*-Δ^1-*p*-menthen-3-one. The formation of the hydroxylamino-oxime is in agreement with this view, since, so far as the author is aware, only substances possessing a double linking in the α-position to the carbonyl group give rise to such compounds. Although it might appear at first sight that the formation of a benzylidene derivative was a cogent argument against such a constitution, yet Wallach (*Annalen*, 1913, **397**, 216) observed that Δ^4-*p*-menthen-3-one gave a dibenzylidene derivative, to which he assigned formula I, and he suggested that the formation of this substance was due to activation of the carbon atom* by the adjacent double linking. A similar argument satisfactorily accounts for the formation of the benzylidene derivative of piperitone, which would then be represented by formula II.


(I.)


(II.)

EXPERIMENTAL.

The oil used for investigation, which had been obtained in a 1 per cent. yield from the grass, was pale yellow in colour and possessed a characteristic smell of peppermint. It had the following constants: $D^{30°}_{30°}$ 0·9203, $n^{30°}_D$ 1·481, $[\alpha]^{30°}_D + 51{\cdot}68°$, acid value 0·7, saponification value 12·0, saponification value after acetylation

47·4,* (vol.) percentage of ketone by absorption with neutral sodium sulphite solution 77.

A quantity of the oil was distilled under diminished pressure (200 mm.), when the following fractions were obtained: (I) up to 160° (20 per cent.), (II) 160—190° (73·2 per cent.), (III) above 190° (6·6 per cent.). These fractions were systematically refractionated at the same pressure and yielded ultimately the following fractions: (i) 115—130° (14·6 per cent.), (ii) 130—174° (1·6 per cent.), (iii) 174—185° (70 per cent.), (iv) 185—205° (12 per cent.).†

Fraction (i).—This fraction consisted essentially of a hydrocarbon (Found: $C = 85{\cdot}8$; $H = 10{\cdot}5$ per cent.) and had the following constants: $D_{30^\circ}^{30^\circ}$ 0·8561, n_D^{30} 1·4736, $[\alpha]_D^{30^\circ} + 59{\cdot}95^\circ$. It was purified by repeated distillation over sodium and finally over sodium in a current of hydrogen. The hydrocarbon then distilled at 101°/100 mm. and at 163—164°/698 mm., and had $D_{30^\circ}^{30^\circ}$ 0·8565, $n_D^{30^\circ}$ 1·474, $[\alpha]_D^{30^\circ} + 54{\cdot}82^\circ$ (Found: $C = 88{\cdot}4$; $H = 11{\cdot}4$. $C_{10}H_{16}$ requires $C = 88{\cdot}2$; $H = 11{\cdot}8$ per cent.). The hydrocarbon possessed a pleasant smell reminiscent of cymene; when it was dissolved in acetic anhydride solution and treated with a drop of concentrated sulphuric acid, a transient purple coloration appeared, which rapidly passed into a deep brown. In chloroform solution it reacted readily with bromine, but after the addition of 1 molecule of bromine the absorption became very slow and hydrogen bromide was evolved. On removing the chloroform in a vacuum, a viscid oil was obtained, which showed no signs of crystallising. Attempts to prepare a crystalline nitrosochloride, nitrosate, and nitrosite were also unsuccessful, only oils being obtained. When the hydrocarbon was treated with hydrogen chloride in ethereal solution, an oil resulted, which was probably a *monohydrochloride* (Found: $Cl = 22{\cdot}9$. $C_{10}H_{17}Cl$ requires $Cl = 20{\cdot}6$ per cent.); with hydrogen bromide in acetic acid solution, a viscous oil was obtained, which was evidently a *dihydrobromide* (Found: Br = 53·8. $C_{10}H_{18}Br_2$ requires Br = 53·8 per cent.); the hydrogen iodide derivative was very unstable, and decomposed even when kept at 0°.

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* As no trace of either esters or alcohols could be detected on chemical examination of the oil, a sample of the pure ketone (from the sodium sulphite compound) was treated in the usual manner for the determination of the saponification value and of the saponification value after acetylation, when the following results were obtained: saponification value 15·3, saponification value after acetylation 36·7. The action of alkali on the ketone has not been investigated, but it is clear that the oil does not contain either esters or alcohols, the apparent saponification value being due to the action of the alkali on the ketone.

† For purposes of comparison a quantity of the oil (100 grams) was shaken with sodium sulphite solution until absorption was complete, when approximately 78 per cent. of the oil was absorbed. The remaining oil was separated and distilled under diminished pressure (200 mm.), when 14 grams of an oil boiling below 130° were obtained. Only 3 grams of an oil boiling above 190° remained, and this still contained traces of the ketone. This method of separation was found to be extremely tedious, as absorption by the sodium sulphite solution was very slow.

The terpene was readily attacked when treated with potassium permanganate at 0° in the presence of alkali. A small quantity of a neutral oxidation product was isolated as a viscous oil which showed no tendency to crystallise. No crystalline acids could be obtained. Further experiments are in progress with a view to determine the constitution of this terpene.

Fraction (ii).—This fraction, which was too small in quantity for detailed examination, consisted apparently mainly of a mixture of *d*-piperitone and the hydrocarbon.

Fraction (iii).—This fraction, which formed the main bulk of the oil, distilled very constantly at 178—181°/200 mm. and was evidently homogeneous (Found: C = 78·2; H = 10·2. $C_{10}H_{16}O$ requires C = 78·9; H = 10·3 per cent.). The following constants were observed: $D_{30°}^{30}$ 0·9321, n_D^{30} 1·481, $[\alpha]_D^{30}$ + 36·76°. It was almost completely absorbed by a neutral sodium sulphite solution, only about 2 per cent. remaining undissolved. A quantity of the ketone was therefore purified by solution in sodium sulphite solution and reprecipitation by alkali, when it was found to boil at 180—181°/200 mm. and at 230—231°/697 mm. (Found: C = 79·1; H = 10·4 per cent.), and to have D_{30}^{30} 0·9307, n_D^{30} 1·481, $[\alpha]_D^{30}$ + 7·92°. Attention has already been directed to the racemisation of *d*-piperitone by alkali. *d*-Piperitone is a colourless, mobile oil with a pronounced odour of peppermint; on standing, it gradually becomes brownish-yellow in colour.

Fraction (iv).—This fraction still contained a considerable quantity of *d*-piperitone. When this was removed by treatment with semicarbazide hydrochloride, the oil remaining was found to be too small in quantity for examination.

d-*Piperitonesemicarbazone.*

For the preparation of the semicarbazone the ketone was mixed with a slight excess of an aqueous solution of semicarbazide hydrochloride, and after the addition of sodium acetate alcohol was added until a clear solution was just obtained. After standing over-night, a copious precipitate of the nearly pure *dl*-α-semicarbazone had crystallised. This was collected (yield 75 per cent.), and after being crystallised twice from acetic acid, in which it was not very readily soluble, was obtained in small, glistening plates which melted at 225—227° (Found: N = 20·4. $C_{11}H_{19}ON_3$ requires

N = 20·1 per cent.). The melting point was found to be somewhat dependent upon the rate of heating, since when introduced into a bath previously heated at 215° the compound decomposed at 230°. The α-semicarbazone was found to be very sparingly soluble in all the ordinary organic solvents and to be optically inactive.

The alcoholic solution from which the α-semicarbazone had separated was diluted with water, when a further quantity of semicarbazone was precipitated. This was purified by repeated crystallisation from alcohol, from which it was ultimately obtained in glistening needles which melted at 193—194°, sintering slightly at 188° (Found: N = 20·3. $C_{11}H_{19}ON_3$ requires N = 20·1 per cent.).

d-*Piperitone*-β-*semicarbazone* appeared to be somewhat more soluble in alcohol than the racemic β-semicarbazone. When exposed to the air in bright sunlight, it rapidly became yellow, but when kept in the dark the colour developed much more slowly. When dissolved in alcohol, the yellow semicarbazone yielded a colourless solution. The *d*-β-semicarbazone was highly active; in pyridine solution $[\alpha]_D^{34^\circ}$ — 216·8° was observed.

dl-*Piperitonesemicarbazones.*

The semicarbazones of the racemic ketone were prepared in the manner described above. The *dl*-α-semicarbazone, after crystallisation from acetic acid, melted at 225—227° (Found: N = 20·2 per cent.). The *dl*-β-semicarbazone separated from alcohol in stellate masses of needles melting at 174—176° and was optically inactive (Found: N = 20·0 per cent.).

d-*Piperitoneoxime and* d-*Piperitonehydroxylamino-oxime Acetate.*

For the preparation of the oxime the method advocated by Lapworth and Steele (T., 1911, **99**, 1884) was adopted. The active ketone (5 grams) was dissolved in alcohol (20 c.c.) and after the addition of hydroxylamine hydrochloride (2·3 grams) and sodium acetate (4 grams) the mixture was heated on the water-bath for five hours. On distillation in steam, almost the whole of the product passed over, only a small quantity of resinous material remaining in the distillation flask. The steam distillate consisted of an oil which, on long standing at 0°, partly solidified. The solid was separated with the aid of the pump, drained on porous porcelain, and recrystallised from dilute methyl alcohol, when it was obtained in lustrous prisms melting at 117—118° (Found:

$N = 8{\cdot}7$. $C_{10}H_{17}ON$ requires $N = 8{\cdot}4$ per cent.). The oxime was optically inactive. The oil from which the solid oxime had been separated was taken up with ether, the ether dried and evaporated and the residual oil distilled under diminished pressure (100 mm. when it distilled almost completely at about 190—195°, yielding a viscid oil which deposited a further trace of the solid oxime on standing. The oil was not further investigated, but consisted possibly of the active oxime. When the calculated quantity of sodium hydroxide was used in place of sodium acetate in the preparation of the oxime, similar results were obtained, the yield of solid oxime being slightly higher. If excess of sodium hydroxide was used, only the solid oxime was obtained, the oily oxime being completely absent.

When *d*-piperitone was treated with a considerable excess of hydroxylamine hydrochloride under conditions similar to those described above, a substance was obtained which was not readily volatile in steam. This was purified by crystallisation from a mixture of methyl alcohol and benzene, when it was obtained in long, thin prisms which decomposed at 156—157° (Found: $C = 55{\cdot}3$; $H = 9{\cdot}2$; $N = 11{\cdot}2$. $C_{12}H_{24}O_4N_2$ requires $C = 55{\cdot}4$; $H = 9{\cdot}2$; $N = 10{\cdot}8$ per cent.). This substance was evidently the *acetate* of d-*piperitonehydroxylamino-oxime.* It was distinctly active and gave in methyl-alcoholic solution $[\alpha]_D^{30^\circ} - 20{\cdot}42^\circ$. Attempts to isolate the *d*-piperitonehydroxylamino-oxime in a crystalline form were unsuccessful.

dl-*Piperitoneoxime and* dl-*Dibromopiperitoneoxime.*

When *dl*-piperitone was treated with hydroxylamine hydrochloride in the manner described above, the product in the steam distillate crystallised completely, no trace of an oil being observed. It was purified by crystallisation from dilute methyl alcohol, when it was obtained in lustrous prisms melting at 117—118° (Found: $N = 8{\cdot}7$ per cent.).

When the oxime was dissolved in chloroform and treated with the calculated quantity of bromine, dl-*dibromopiperitoneoxime* was readily obtained. It crystallised from alcohol in prisms, or from a dilute solution in cubes, which decomposed at 141° (Found: $Br = 48{\cdot}6$. $C_{10}H_{17}ONBr_2$ requires $Br = 48{\cdot}9$ per cent.).

dl-*Piperitonehydroxylamino-oxime.*

On treatment with excess of hydroxylamine hydrochloride in the manner described by Read and Smith (*loc. cit.*, p. 783) *dl*-piperitonehydroxylamino-oxime was obtained. After crystallisation from a mixture of alcohol and ether, it melted at 170—171° and gave all the colour reactions mentioned by these authors (Found : C = 59·6; H = 10·1. Calc., C = 59·9; H = 10·1 per cent.).

Benzylidene-dl-*piperitone.*

This substance was prepared in the manner described by Read and Smith (*loc. cit.*, p. 785). It melted at 61° and had all the properties recorded by these authors (Found : C = 84·4; H = 8·4. Calc., C = 84·9; H = 8·4 per cent.). Although prepared from the optically active ketone, it was found to be inactive.

Oxidation of d-*Piperitone.*

I. *With Ferric Chloride.*—When *d*-piperitone was heated on the water-bath with excess of ferric chloride in acetic acid solution, thymol was obtained in a yield of about 25 per cent. The thymol obtained melted at 50—51° and was identified by the method of mixed melting point and by the usual tests.

II. *With Potassium Permanganate.*—In one experiment *d*-piperitone (50 grams) was mixed with dilute sodium hydroxide solution and treated with a 5 per cent. solution of potassium permanganate at 0° until no further action took place. The solution was filtered, concentrated, and acidified, when a viscous oil separated. This was taken up with ether, the ether dried and evaporated, and the residual oil esterified in the usual manner. The ethyl ester thus obtained distilled mainly at 170—180°/53 mm. and consisted apparently of nearly pure ethyl *l*-γ-acetyl-α-*iso*propylbutyrate, since on analysis it gave figures agreeing approximately with this formula (Found : C = 64·6; H = 9·4. Calc., C = 67·3; H = 9·5 per cent.). The ester was found to be slightly active, $[\alpha]_D^{30^\circ}$ — 5·58°. The above view of the constitution was confirmed by the preparation of the *semicarbazone*, which separated from dilute alcohol in woolly needles melting at 115° (Found : N = 16·1. $C_{12}H_{23}O_3N_3$ requires N = 16·3 per cent.). The crude ester was hydrolysed with alcoholic potassium hydroxide solution and the resulting acid distilled under diminished pressure (48 mm.), when the main portion distilled at 195—200° and consisted of apparently pure *l*-γ-acetyl-α-*iso*propylbutyric acid (Found : in the silver salt, Ag = 38·8. Calc., Ag = 38·7 per cent.). The semicarbazone, prepared in the usual manner, separated as an oil which rapidly solidified. It was purified by repeated crystallisation from hot water containing a little alcohol, when it was obtained in balls of needles melting at 150—

152°, the melting point depending somewhat on the rate of heating (Found: N = 18·5. Calc., N = 18·3 per cent.). When the compound was treated with sodium hypobromite solution at 0°, a quantitative yield of α-*iso*propylglutaric acid was obtained. This acid, after crystallisation from hydrochloric acid, melted at 94—95° (Found: C = 55·4; H = 7·8. Calc., C = 55·2; H = 8·0 per cent.). The acid was found to be optically inactive. The identity of the acid was confirmed by the preparation of the anhydride, which crystallised in needles resembling glass-wool, melted at 53—54°, and gave an anil melting at 158° (compare Perkin, *loc. cit.*).

In conclusion, the author wishes to thank his assistants, Mr. Gopal Rau and Mr. Ghose, for making the analyses.

THE FOREST RESEARCH INSTITUTE,
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[*Received, August* 23*rd*, 1921.]

CLXXXVIII.—*The Calculation of the Colour of "Cyclic" Coloured Substances.*

By JAMES MOIR.

FOR the purpose of this paper, a "cyclic" coloured substance is to be considered as one which possesses a sharp absorption band caused in some manner by an "active" ring existing in the substance. A ring is "active" if it bears, in any position, an ionisable group of the auxochrome type, namely, OH, NH_2, NHMe, etc.

The position of the absorption band may vary between λ 100 and λ 1600 micromillimetres. Some "cyclic" coloured substances, therefore, may appear to be colourless to the eye, which only detects colours the bands of which lie above λ 350 and below λ 770.

If only one of the rings present in a compound is "active," it is classed as a "monocyclic" coloured substance. In a certain sense, phenol in the presence of alkali and aniline in the presence of acid comply with this definition, but as a rule the absorption band is not fully developed (visible in very great dilution) unless another atom of some kind is attached to the active ring, as, for example, in saligenin and benzoquinone.

Coloured substances with more than one "active" ring are all classed as "dicyclic."* The simplest type of the linking of two active rings occurs in benzhydrols and indamines. In the more complex types, there are two linking atoms uniting the active rings, as in the oxazines, fluoresceins, acridines, etc.

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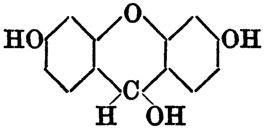
* See page 1663.

Some examples will serve to make these definitions clear. Thus hydroxybenzhydrol, $C_6H_5\cdot CH(OH)\cdot C_6H_4\cdot OH$, is monocyclic because the simple phenyl ring is not active, whereas dihydroxybenzhydrol, $HO\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot OH$, and dihydroxyxanthhydrol,



are "dicyclic," the active rings of the former being singly linked, by —CH(OH)—, and of the latter doubly linked, by —CH(OH)— and —O—.

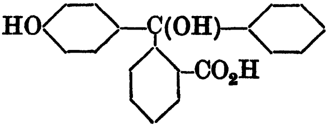
The author has discovered that the position of the absorption band can be calculated from the constitutional formula of the substance in all these cases. The calculation consists merely in multiplying a fundamental wave-length (which is that of the absorption band of the parent-substance) by a number of factors, each of which is constant and characteristic of the group or radicle to which it belongs. This may be expressed by the equation:

$$\lambda_x = k_1 k_2 \ldots . k_n \lambda_0,$$

in which λ_0 is the wave-length of the absorption band of the parent-substance, λ_x that of the substance to be calculated, k_1 the colour-factor (say) for phenyl if the substance is a phenyl derivative of the parent-substance, k_2 the colour-factor for another group or atom (for example, bromine or carboxyl) present in the substance, and so on.

For the monocyclic series, the parent-substance may be taken to be *p*-hydroxybenzyl alcohol, of which the anhydride is quinomethane (methylene-*p*-benzoquinone). This is assumed to have $\lambda_0 = 290$. I have not observed it, but the phenoxide ion has λ 286 and the *p*-tolyloxide ion λ 287 * in aqueous solution.

The colour of hydroxydiphenylphthalide, as an example of a monocyclic coloured substance, may be calculated. When the formula is written in its hydroxylated form to avoid quinonoid linkings,



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* Baly and Ewbank (T., 1905, 87, diagrams on pp. 1350 and 1352) find λ 290 and 291 in alcohol. The difference is due to the sodium not being ionised.

the substance is seen to be *p*-hydroxybenzyl alcohol, in which two phenyl groups are substituted for the methylene hydrogen atoms and a carboxyl group is substituted for a hydrogen atom in an *ortho*-position in one of these phenyl groups. The calculation is:

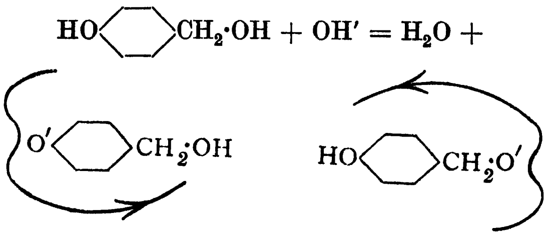
$$\underset{\lambda_0.}{\lambda_x = 290} \times \underset{\text{Phenyl colour-factor, twice.}}{1\cdot135 \times 1\cdot135} \times \underset{o\text{-Carboxyl colour factor.}}{1\cdot055} = 394\cdot2$$

This agrees exactly with the observed value; the latter is accurate only to one unit, so that the fraction in the calculated value may be neglected.

In order to visualise properly such a factorial scheme of colour, it is necessary to put forward a new provisional theory of colour which shall serve as a physical basis for the factorial property.

What I suggest is that a charged particle (electron or other negatively charged group, such as OH′), exists in all these substances and constantly describes an orbit round the active part of the molecule. Since none of the molecules is perfectly circular and symmetrical, the periodic time of the particle in the orbit will be subject to perturbations; that is to say, it will have a constant average value, yet individual circuits of the orbit will take place in slightly different times. This produces an absorption band, which is not sharp like that of the vapour of a metal, but is diffuse on both sides of the average, sometimes unsymmetrically.

It is probable that in the monocyclic class the orbit is almost circular, with a kink at the two places where the electron could stop if the substance were not ionised. The following is an attempt to give a visual impression of my meaning.



(I.) (II.)

This conception explains well how any addition to the parent-substance must expand the orbit, since the added groups must lie outside the orbit and therefore attract the electron further from the centre,* and so increase the periodic time and thus the wave-length of the absorption.

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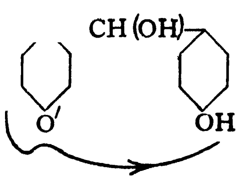
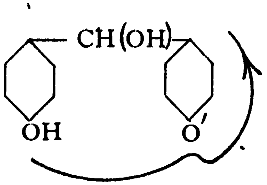
* In astronomy, the periodic time varies as $r^{\frac{3}{2}}/m^{\frac{1}{2}}$, where r is the radius of the orbit and m the attracting mass.

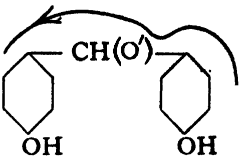
In the dicyclic compounds, the orbit, extending completely round the active part of the molecule, is elliptic and of approximately twice the size; consequently the periodic time is almost double. It is less than double because the attracting mass has been increased, as well as the size of the orbit. Taking *pp'*-dihydroxybenzhydrol as the simplest dicyclic substance, the following diagram approximately represents the motion, with three kinks in the orbit.



(I.)

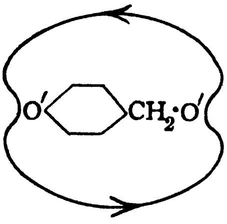


(II.)

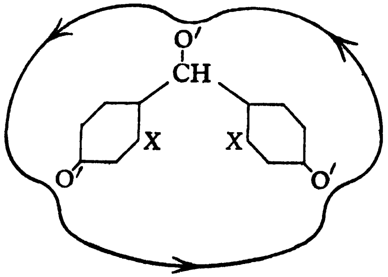


(III.)

The following figures represent my conception of the complete orbits, allowing for the fact that the rings in dihydroxybenzhydrol are most likely inclined to one another at the tetrahedral angle of 109°.



λ 290.



λ 539 when X is hydrogen.

Now, experiment shows that when a dicyclic substance is doubly linked (that is, when the two positions marked X are united by O, NH, S, etc.) the colour becomes lower in a constant proportion for a given linking. Thus :

$$\frac{\lambda_{\text{fluorescein}}}{\lambda_{\text{phenolphthalein}}} = \frac{\lambda_{\text{resorufin}}}{\lambda_{\text{indophenol}}} = 0{\cdot}89\,;\ ^{*}$$

this is the value of the factor for the oxo-linking, —O—.

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* I have investigated ten cases of this sort, giving an average of 0·891 for the oxo-linking factor, with very little variation.

I therefore supplement the above conception of the dicyclic orbit with the supposition that a second linking draws the two rings closer together and so contracts the orbit in constant proportion for a given linking, making it more circular and therefore leading to a smaller absorption wave-length.

In general, it may be noted that this orbit theory bears a considerable resemblance to the theories of Hewitt and of Watson and Meek of the three and five tautomerisms, for most of their three-tautomerism substances are "monocyclic," and my "dicyclic" substances can be written so as to exhibit five tautomerisms more frequently than any other number.

Method of Calculating the Colour of Dicyclic Substances.

This follows immediately from the above theory. Two phenol rings taken together form the "parent-substance" and the constant fundamental absorption wave-length λ 1380 is assigned to this combination. This figure is multiplied by the linking-factors of the group or groups joining the rings.

The product is the absorption wave-length of the *prototype* of the coloured substance under consideration, that is, dihydroxybenzhydrol if the linking group is CH·OH, indophenol if the linking group is NOH, resorufin if there are the two linking groups, NOH and O, and so on.

This prototype wave-length is then multiplied by the "colour-factors" corresponding with all the side-groups or inactive rings in the molecule, and the product is the absorption wave-length of the coloured substance.

Thus, to calculate the colour of fluorescein, λ 1380 is multiplied first by 0·39 ("hydroxymethylene-linking factor"). The product λ 539 is the absorption wave-length of *pp'*-dihydroxybenzhydrol. This is then multiplied by 0·891 ("oxo-linking factor"); the product λ 480 is the absorption wave-length of 3 : 6-dihydroxyxanthhydrol, which is the *prototype* of fluorescein. Fluorescein is the *ortho*-benzoic acid derivative of 3 : 6-dihydroxyxanthhydrol, and the calculation is completed by multiplying λ 480 by the benzoic acid colour-factor,* which, as it represents a "load" outside the orbit, is greater than unity, namely, 1·029. Hence fluorescein has $\lambda_x = 480 \times 1{\cdot}029 = 494{\cdot}5$. Representing the whole calculation by one equation, we have $\lambda_x = 1380 \times 0{\cdot}39 \times 0{\cdot}891 \times 1{\cdot}029 = 494{\cdot}5$. This agrees with the observed value (λ 493·5 to 494).

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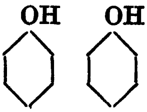
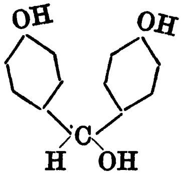
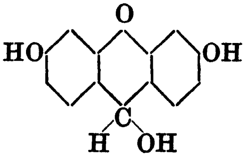
* The benzoic acid factor 1·029 may itself be resolved into a phenyl factor (1·026) and an *ortho*-carboxyl factor (1·003). Using the former with λ 480 of dihydroxyxanthhydrol, we get the colour of phenyldihydroxyxanthhydrol (resorcinolbenzein) = λ 493 as another intermediate stage on the way to fluorescein.



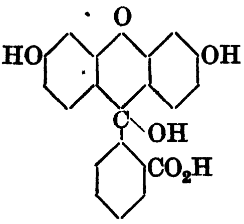
Two phenol rings.
λ 1380.



Dihydroxybenzhydrol.
Obs. λ 539 (calc. λ 538).

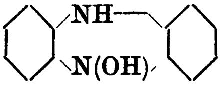
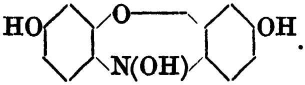


Dihydroxyxanthhydrol.
Obs. λ 479 (calc. λ 480).



Fluorescein.
λ 494.

The factors may be combined in any order; thus, to calculate the colour of fluorescein, that of phenolphthalein may first be calculated (λ 1380 × 0·39 × 1·029 = λ 555) and its wave-length finally multiplied by the oxo-linking factor 0·891.

For the purpose of these calculations it is necessary to write all constitutional formulæ in their most hydroxylated form, eliminating quinonoid bonds, para-linkings, and lactone rings. Thus, for example, phenazine is written  and resorufin . It is a deduction from such a theory that the colour of dicyclic substances comes down from the infra-red with increasing complexity of linking, not up from the ultra-violet, as is usually supposed. On the other hand, increasing complexity *outside* the linkings puts the colour up again, as is well known.

Returning to the monocyclic coloured substances, I now append a table, giving the value of the colour-factors.

Monocyclic Colour-factors.

Name of factor.	Property of factor.	Numerical value.
A. Phenyl	$CH_2 \cdot OH \longrightarrow PhCH \cdot OH \longrightarrow Ph_2C \cdot OH$	1·135
B. *ortho*-Carboxyl	Phenyl compound $\longrightarrow$ phthalein	1·055
C. Phthalein	$\cdot C_6H_4 \cdot CO_2H$ introduced into a carbinol	1·200†
D. Amino-	Calculation of aniline derivatives from phenol derivatives	1·140
E. *N*-methyl	Calculation of methylamino- and dimethylamino-compounds from amino-compounds	1·035
F. Methylamino-	Calculation of methylamino-compounds from hydroxyl compounds	1·180‡
G. Dimethylamino-	Calculation of dimethylamino- from hydroxyl compounds	1·222‡

† This is factor A × factor B. Third places of decimals are estimates.
‡ These are D × E and D × E^2.

The next table gives the results of applying these factors.

The Calculated Colours of Monocyclic Substances.

Name. §	Relation to *p*-hydroxybenzyl alcohol.	Detailed calculation.	Colour. Calc.	Colour. Obs.
1. Fuchsone	Two phenyl groups	$\lambda\ 290 \times (1{\cdot}135)^2$	λ 374	λ 380 (alc.)
2. Fuchsone-imonium salts	Two phenyl groups, also NH_2 *vice* OH	$\lambda\ 290 \times (1{\cdot}135)^2 \times 1{\cdot}140$	λ 426	λ 425
3. Fuchsonedimethylimonium salts	Two phenyl groups, also NMe_2 *vice* OH	$\lambda\ 290 \times (1{\cdot}135)^2 \times 1{\cdot}222$	λ 457	λ 455
4. Hydroxyphenylphthalide	Factor C	$\lambda\ 290 \times 1{\cdot}20$	λ 348	λ 350
5. Hydroxydiphenylphthalide	Factors A and C	$\lambda\ 290 \times 1{\cdot}135 \times 1{\cdot}20$	λ 394	λ 395
6. Dimethylaminodiphenylphthalide ...	Factors A, C, and G	$\lambda\ 290 \times 1{\cdot}135 \times 1{\cdot}222 \times 1{\cdot}20$	λ 483	λ 480
7. Dimethylaminobenzhydrol	Factors A and G	$\lambda\ 290 \times 1{\cdot}135 \times 1{\cdot}222$	λ 401	λ 400

NOTE.—All the observations recorded in this table (except the first) were made with aqueous solutions in order to get complete ionisation.

§ The formulæ of these compounds are given at the end of the paper.

These constitute about half the possible derivatives of *p*-hydroxybenzyl alcohol; the remaining six have bands in the ultraviolet only, and means for their examination are not at my disposal. I venture, however, to predict their absorption bands, namely,

p-Aminobenzyl alcohol	(weak aqueous acid)	λ 330
p-Dimethylaminobenzyl alcohol	(„ „ „)	λ 354
p-Hydroxybenzhydrol	(weak aqueous alkali)	λ 329
4-Hydroxyphthalide	(„ „ „)	λ 307
p-Aminobenzhydrol	(weak aqueous acid)	λ 375
4-Aminophthalide	(„ „ „)	λ 350

The rough prediction can also be made that the corresponding *ortho*-derivatives, for example, saligenin and *o*-hydroxybenzhydrol, will have bands at about 30 units higher than the *para*-derivatives.

Two future extensions of the theory in respect to monocyclic coloured substances can be pointed out: (1) the active ring may be derived from thiophen, furan, pyrrole, naphthalene, etc., as well as from benzene, (2) the secondary group need not be $-CH_2·OH$, but by analogy may be $-NH·OH$ (giving the quinoneimine family; hydroxylated form), or $-O·OH$ (giving the quinone family), or $-S·OH$ (giving an unknown group [thioquinone]). It is to be noted that all "monocyclic" colours are yellow or orange (λ less than 500).

Part II. Details of the Calculation of the Colour of Dicyclic Compounds.

For this calculation two tables are required, one giving the linking-factors which contract the orbit, and the other the group colour-factors which expand the orbit.

Table of Linking-factors.

	Name.		Numerical value.
A.	Methylene	$-CH_2-$	0·650*
B.	Methenyl	$>CH-$	0·645 (for triphenylcarbinol colours)
C.	Imino-	$-NH-$	0·780*
D.	Oxo-	$-O-$	0·891
E.	Thio-	$-S-$	0·920*
F.	Hydroxymethylene	$-CH(OH)-$	0·390
G.	Keto-	$-CO-$	0·235
H.	Hydroxymethenyl	$>C(OH)-$	0·387 (for triphenylcarbinol colours)
I.	Oximino-	$-N(OH)-$	0·470*
[J.	Sulphoxide	$-SO-$	0·55 (inferred, not experimental)]

* The third place of decimals is as yet provisional in these cases.

I have worked out about thirty group-colour-factors, of which the most important are given below.†

Table of Dicyclic Group-colour-factors.

1. NH_2/OH = 1·007 (used to calculate aniline colours from phenol colours)
2. $NHMe/OH$ = 1·035 (,, ,, methylaniline ,, ,, ,,)
3. NMe_2/OH = 1·059 (,, ,, dimethylaniline ,, ,, ,,)
4. NEt_2/OH = 1·061 (,, ,, diethylaniline ,, ,, ,,)
5. $NHPh/OH$ = 1·060 (,, ,, diphenylamine ,, ,, ,,)
6. $NHPh/NH_2$ = 1·052 (substitution of Ph for H in an "active" amino-group)
7. $\left.\begin{array}{l}CPh/CH\\NPh/NH\end{array}\right\}$ = 1·026 (substitution of Ph for H in *any linking* group)
8. $C_6H_4·CO_2H/H$ = 1·029 (used to calculate phthalein and rhodamine colours from those of hydrols)
9. $C_6H_4·SO_3H/H$ = 1·045 (used to calculate sulphonephthalein colours from those of hydrols)

$$\left.\begin{array}{ll}10. & \textit{ortho}\text{-}CH_3\\ 11. & \textit{ortho}\text{-}Et\\ 12. & \textit{ortho}\text{-}Cl\\ 13. & \textit{ortho}\text{-}Br\end{array}\right\} = 1·013 \left\{\text{used for substituents } \textit{ortho} \text{ to the active group}\right\}$$

14. *meta*-Groups = 1·026 (,, ,, ,, *meta* ,, ,, ,,)

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† Most of the remainder are to be found in A., 1921, **120**, ii, 6, where "*N*-ethyl 1·023" should read "NEt_2 1·023." Note should also be taken that the figures in the abstract refer to substitution of a group for hydrogen, whereas in this paper substitution for hydroxyl is the basis of calculation.

It is to be most carefully noted that these factors only apply to the dicyclic group. The monocyclic factors (page 1660) are much larger than these.

*Calculation of the Colour of Familiar Dicyclic Substances.**

A.—The simplest dicyclic substances are those with only one linking group.

			Obs. (in water).
1. *pp'*-Dihydroxybenzhydrol contains the linking F......	$\lambda_x = 1380 \times 0{\cdot}39$	$= 538$	λ 539
2. Michler's carbinol is the foregoing with NMe_2 for OH (twice)	$\lambda_x = 1380 \times 0{\cdot}39 \times (1{\cdot}059)^2$	$= 603$	λ 603
3. Michler's ketone is the foregoing with linking G for F	$\lambda_x = 1380 \times 0{\cdot}235 \times (1{\cdot}059)^2$	$= 363$	λ 364
4. Indophenol contains the linking I	$\lambda_x = 1380 \times 0{\cdot}47$	$= 649$	λ 650
5. Bindschedler's green contains the linking I and two NMe_2 groups	$\lambda_x = 1380 \times 0{\cdot}47 \times (1{\cdot}059)^2$	$= 728$	λ 730
6. Indamine contains the linking I and two NH_2 groups	$\lambda_x = 1380 \times 0{\cdot}47 \times (1{\cdot}007)^2$	$= 658$	λ 660

Nearly all the other possible, singly-linked, dicyclic substances will be found on calculation to have colours in the infra-red, for example, dihydroxydiphenylmethane λ 897, quinol hemi-ether λ 1225, and dihydroxydiphenylamine λ 1075.

A few others, like *pp'*-dihydroxybenzophenone (calculated λ 324), are coloured in the ultra-violet. I hope that some one will measure the absorption bands of these substances so that it may be ascertained whether the theory still holds in these extreme cases.

B.—The next simplest are prototype, doubly-linked substances, that is, those constituted of only two linking groups and the active rings.

			Obs. (in water).
7. Dihydroxyxanthhydrol has linkings D and F	$\lambda_x = 1380 \times 0{\cdot}39 \times 0{\cdot}891$	$= 479$	λ 479
8. Dihydroxyacridine has linkings C and F	$\lambda_x = 1380 \times 0{\cdot}39 \times 0{\cdot}78$	$= 420$	λ 421
9. Dihydroxyphenazine has linkings C and I	$\lambda_x = 1380 \times 0{\cdot}78 \times 0{\cdot}47$	$= 506$	λ 510
10. 2 : 7-Dihydroxyanthracene has linkings A and F	$\lambda_x = 1380 \times 0{\cdot}65 \times 0{\cdot}39$	$= 350$	? †
11. Resorufin has linkings D and I	$\lambda_x = 1380 \times 0{\cdot}89 \times 0{\cdot}47$	$= 577$	λ 576
12. Thionol has linkings E and I...	$\lambda_x = 1380 \times 0{\cdot}92 \times 0{\cdot}47$	$= 596$	λ 593
13. Pyronine is No. 7 with $2NMe_2$ for 2OH	$\lambda_x = 479 \times (1{\cdot}059)^2$	$= 537$	λ 537
14. Methylene-blue is No. 12 with $2NMe_2$ for 2OH	$\lambda_x = 596 \times (1{\cdot}059)^2$	$= 668$	λ 667 + λ 606
15. Ethylene-blue is No. 12 with $2NEt_2$ for 2OH	$\lambda_x = 596 \times (1{\cdot}061)^2$	$= 672$	λ 673

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* The formulæ of these compounds are given at the end of the paper.

† See "Rufol" (Beilstein, "Organische Chemie," II, 999), which has the required colour.

C.—The next simplest are triphenylcarbinol and phenazine dyes in which one ring is inactive, namely, the benzeins, phthaleins, rhodamines, "sulphonephthaleins," safranines, benzoflavines, etc.

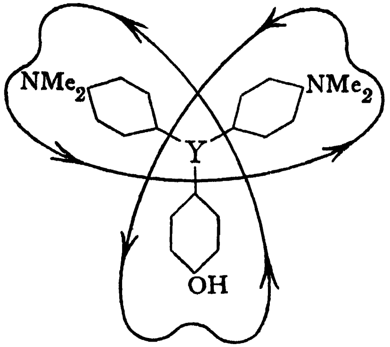
			Obs. (in water).
16. Benzaurin is the phenyl derivative of No. 1 ...	$\lambda_x = 538 \times 1{\cdot}026$	$=553$	λ 553
17. Phenolphthalein is the $C_6H_4{\cdot}CO_2H$ derivative of No. 1	$\lambda_x = 538 \times 1{\cdot}029$	$=555$	λ 554
18. Tetrabromobenzaurin has 4Br all *ortho* to OH	$\lambda_x = 553 \times (1{\cdot}013)^4$	$=583$	λ 583
19. Malachite-green is the phenyl derivative of No. 2 ...	$\lambda_x = 603 \times 1{\cdot}026$	$=619$	λ 619
20. Brilliant-green is the tetraethyl derivative............	$\lambda_x = 619 \div (1{\cdot}059)^2 \times (1{\cdot}061)^2$	$=623$	λ 622
21. Rhodamine is the $C_6H_4{\cdot}CO_2H$ derivative of No. 13	$\lambda_x = 537 \times 1{\cdot}029$	$=552$	λ 553
22. Doebner's violet is No. 16 with $2NH_2$ for 2OH	$\lambda_x = 553 \times (1{\cdot}007)^2$	$=561$	λ 562
23. Safranine is phenyldiaminophenazine (see No. 9)	$\lambda_x = 506 \times (1{\cdot}007)^2 \times 1{\cdot}026$	$=527$	λ 525 + λ 505
24. Benzoflavine is phenyldiaminoacridine (see No. 8)	$\lambda_x = 420 \times (1{\cdot}007)^2 \times 1{\cdot}026$	$=437$	λ 450*
25. Eosine is No. 17 with the oxo-linking and 4Br	$\lambda_x = 555 \times 0{\cdot}891 \times (1{\cdot}013)^4$	$=521$	λ 521
26. Thymolsulphonephthalein is No. 1 with $C_6H_4{\cdot}SO_3H$, $2CH_3$ (*meta*) and $2C_3H_7$ (*ortho*) ...	$\lambda_x = 538 \times 1{\cdot}045 \times (1{\cdot}026)^2 \times (1{\cdot}013)^2$	$=607$	λ 604

* Commercial specimen, possibly containing methyl groups.

It is to be noted that the factors can be multiplied and divided mutually, giving new factors for special purposes. Thus a special safranine factor is obtained by multiplying the NH, the NOH, and the Ph factors together and dividing by the PhC(OH) factor (1·026 × 0·39). This gives 0·94, by means of which the colour of any safranine can be calculated from that of the corresponding benzaurin.

In this way, for example, the indulines and nigrosines can be correlated with the phenyl dye analogous to malachite-green.

D.—The remaining class has three rings, all of which are active, but owing to the attraction of the central carbinol hydroxyl group an orbit round the whole molecule is unstable, so that instead of *such an orbit, a looped or trefoil orbit is performed by the moving particle, and only two rings at a time act.*



Where Y = C(OH).

This assumption is necessary to explain why the three symmetrical substances aurin, pararosaniline, and crystal-violet have colours which are very close to those of dihydroxybenzhydrol, diaminobenzhydrol, and Michler's carbinol.

The factor H (" hydroxymethenyl ") of value 0·387 is used here :

		Obs. (in water).
27. Aurin : *Two* phenol rings...	$\lambda_x = 1380 \times 0{\cdot}387 = 534$	λ 534
28. Pararosaniline : *Two* aniline rings	$\lambda_x = 1380 \times (1{\cdot}007)^2 \times 0{\cdot}387 = 542$	λ 543
29. Crystal-violet : *Two* dimethylaniline rings	$\lambda_x = 1380 \times (1{\cdot}059)^2 \times 0{\cdot}387 = 598$	λ 596
30. Aniline-blue : *Two* diphenylamine rings	$\lambda_x = 1380 \times (1{\cdot}060)^2 \times 0{\cdot}387 = 600$	λ 601

Since the hydroxymethylene factor F is 0·390, the relation to the benzhydrol colours is thus brought out, the orbits being almost identical.

This new theory with respect to substances with *three* active rings requires that such a substance as "*p*-hydroxy-malachite-green" (formula above) shall exhibit two colours simultaneously. This is in accordance with fact. This substance is purple, with λ 578, when faintly alkaline, and blue, with λ 608, when faintly acid, and shows both bands when neutral; the lower band is close to the position of the band of hydroxydimethylaminobenzhydrol, and the upper band is close to the position of the band of bisdimethylaminobenzhydrol (λλ 571 and 603 respectively). Therefore, when the substance is neutral, it has the trefoil orbit and shows both bands; when it is acid, the $-C_6H_4{\cdot}OH$ group is suppressed and the substance has the same orbit as Michler's carbinol; when it is alkaline, one $-C_6H_4{\cdot}NMe_2$ group is suppressed and the substance behaves almost as if it were hydroxydimethylaminobenzhydrol.

In the same way, the green colour (λ 632) of acid crystal-violet is explained: one of the groups is no longer active, but becomes $-C_6H_4{\cdot}NHMe_2Cl$, the orbit becomes much the same as that of malachite-green, and the colour is that of a " loaded " malachite-green. Finally, if much acid is present, two of the groups become $-C_6H_4{\cdot}NHMe_2Cl$ and the substance then contains only *one* active ring and is monocyclic and yellow (observed λ 420). Similarly, acid malachite-green is yellow and is monocyclic (observed λ 438).

Other substances, such as oxyhæmoglobin and carmin, which exhibit double-banded colours will probably be shown to be capable of similar alternative orbits.

Some notes on the extension of the theory are now appended.

1. As a rule, the position of the absorption band is very slightly affected if the active groups are not in the *para*-position with respect to the linking group. Taking λ 1380 as the value of two *p*-hydroxyphenyl rings, the value for two *m*-hydroxyphenyl rings lies between λ 1385 and λ 1390, and the value for one *para*- with one *ortho*-ring is about λ 1395. An example of the former is quinolphthalein, which is isomeric with fluorescein but has the hydroxyl groups in the *meta*-position with respect to the linking hydroxymethenyl group and has λ 499 (with a faint *blue* fluorescence) in sodium hydroxide solution and rather lower in ammonia.* An example of the *ortho-para*-grouping is phenol-*p*-cresolphthalein, which has λ 572, whilst phenol-*o*-cresolphthalein (which is a *pp'*-compound) has λ 562.

2. The calculation of the colour of naphthol and naphthylamine dyes gives irregular results, but I am of opinion that this is the fault, not of the theory, but of the constitutions assigned to the defaulting substances, one of which, for example, has recently been shown to be an *oo'*- instead of a *pp'*-compound.† The naphthol/phenol factor is in any case very high, varying between 1·08 and 1·14.

3. The factors of linking groups containing oxygen, such as CH·OH, NOH, are related to those of the corresponding non-oxygenated groups by the fraction $\frac{3}{5}$. This probably represents an undiscovered law of nature in connexion with electron movements. The number of fundamental factors can thus be reduced to four, namely, those corresponding with CH_2, NH, O, and S, and the formula of any coloured compound is therefore most simply written, for the purpose of this paper, as that of its leuco-compound

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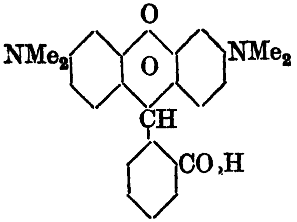
* Fluorescein has λ 494.

† α-Naphtholphthalein (*Ber.*, 1920, **53**, [*B*], 1445).

with the addition of an unbound oxygen atom, the value of the

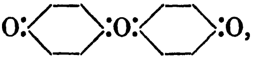
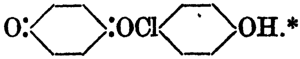


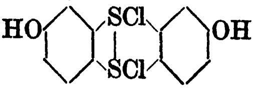
latter being counted as $\frac{3}{5}$ in the calculation; for example, rhodamine: two dimethylaniline rings = $\lambda\,1380 \times (1{\cdot}059)^2 = \lambda\,1547$: the ·O· and ·$CH_2$· linkings lead to multiplying by 0·891 and by 0·65, giving λ 896. This is then multiplied by the benzoic factor and by $\frac{3}{5}$, giving $\lambda\,896 \times 1{\cdot}029 \times 0{\cdot}6 = \lambda\,552$ (see No. 21).

It does not necessarily follow, however, that the leuco-compounds themselves possess sharp absorption bands.

Possible New Classes of Coloured Substances.

(1) Dihydroxydihydroanthracene gives λ 583 by the theory, but as it is a leuco-compound it may not be capable of exhibiting this colour.

(2) Quinol–ether oxide,  should have λ 735 and may possibly exist as a (green) salt, * The existence of similar compounds with S and S:O as the linking groups is possible, and also of isomerides with *m*-hydroxyl groups (resorcinol–ether oxide, etc.).

(3) The compound  also gives a calculated colour (λ 702) lying within the visible spectrum.

(4) 2 : 7- (instead of 3 : 6-)Isomerides of the oxazine, acridine, and thiazine dyes appear to be unknown, but it is to be expected that they would be valuable dyes with slightly higher colours than the 3 : 6-isomerides and would exhibit scarcely any fluorescence.

The Two Exceptions.—(*a*) 3 : 6-Dihydroxyxanthone is described as having λ 381 (E. R. Watson, "Colour and Chemical Constitution," p. 88), whereas the theory gives λ 288. It is possible that the colour was observed in the absence of alkali, in which case the result would be abnormal, as in the case of phenol, the spectrum of which is different from that of the phenoxide ion.

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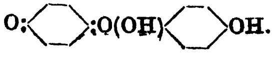
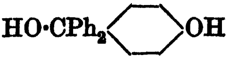
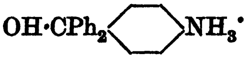
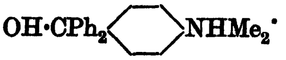
* Compare quinhydrone as 

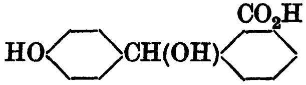
(*b*) 2 : 7-Dihydroxyanthraquinone has a high colour, whereas the theory predicts a value of λ smaller than 100. Probably, when two carbonyl groups are present, they co-operate in producing a special vibration quite different from that produced by one carbonyl group.

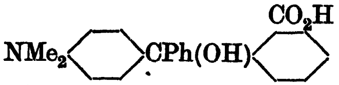
Hydroxylated Formulæ of the Substances dealt with in the Paper (excepting those given in the text).

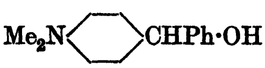

Fuchsone.

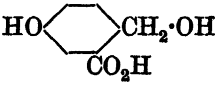

Fuchsoneimonium ion.


Fuchsonedimethylimonium ion.


p-Hydroxyphenylphthalide.


p-Dimethylaminodiphenylphthalide.


p-Dimethylaminobenzhydrol.


4-Hydroxyphthalide.

$HO\cdot CH(C_6H_4\cdot NMe_2)_2$

Michler's carbinol.
Bisdimethylaminobenzhydrol.

$CO(C_6H_4\cdot NMe_2)_2$

Michler's ketone.

$HO\cdot N(C_6H_4\cdot OH)_2$

Indophenol.

$HO\cdot N(C_6H_4\cdot NH_2)_2$

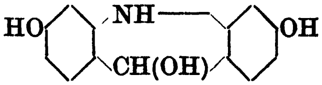
Indamine.

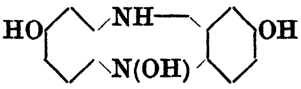
$HO\cdot N(C_6H_4\cdot NMe_2)_2$

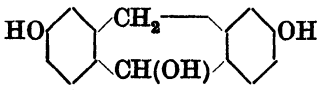
Bindschedler's green.

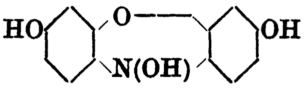
$O(C_6H_4\cdot OH)_2$

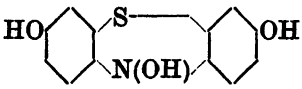
Quinol hemi-ether.

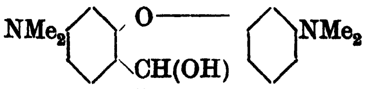

Dihydroxyacridine.

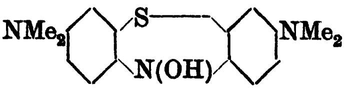

Dihydroxyphenazine.

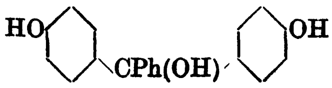

Dihydroxyanthracene.

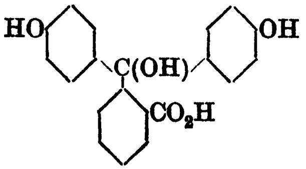

Resorufin.

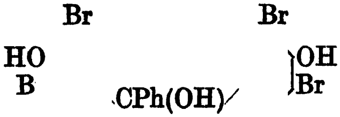

Thionol.


Pyronine.


Methylene-blue.


Benzaurin.


Phenolphthalein.



Tetrabromobenzaurin.

$HO\cdot CPh(C_6H_4\cdot NMe_2)_2$

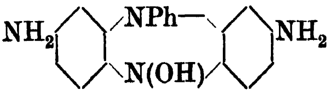
Malachite-green.

$OH\cdot CPh(C_6H_4\cdot NEt_2)_2$

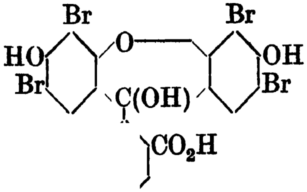
Brilliant-green.

$OH\cdot CPh(C_6H_4\cdot NH_2)_2$

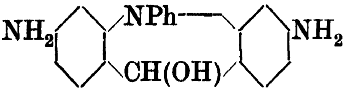
Döbner's violet.



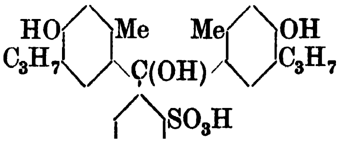
Safranine.
(or with NPh and NOH reversed.)



Eosine.



Benzoflavine.



Thymolsulphonephthalein.

$OH\cdot C(C_6H_4\cdot OH)_3$

Aurin.

$OH\cdot C(C_6H_4\cdot NH_2)_3$

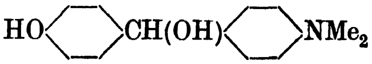
Pararosaniline.

$OH\cdot C(C_6H_4\cdot NMe_2)_3$

Crystal-violet.

$OH\cdot C(C_6H_4\cdot NHPh)_3$

Aniline-blue.



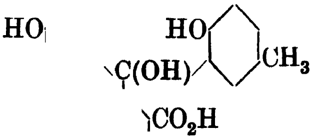
Hydroxydimethylaminobenzhydrol.

$(C_6H_4\cdot NMe_2)_2C(OH)\cdot C_6H_4\cdot NHMe_2^{\cdot}$

Crystal-violet ion (green) in
moderately acid solution.

$NMe_2\cdot C_6H_4\cdot C(OH)(C_6H_4\cdot NHMe_2)_2^{\cdot\cdot}$

Crystal-violet ion (yellow)
in strongly acid solution.



Phenol-*p*-cresolphthalein.

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JOHANNESBURG.

[*Received, February* 17*th*, 1921.]

CLXXXIX.—*The Hydration of the Fibres of Soap Curd. Part III. Sorption by Sodium Palmitate.*

By Mary Evelyn Laing.

Previous work (McBain and Taylor, T., 1919, **115**, 1300; McBain and Martin, this vol., p. 1369; McBain and Salmon, *ibid.*, p. 1374) has shown that the fibres which form the structural basis of soap curd abstract by their hydration definite amounts of water from the solution with which they are in contact and thus give rise to the appearance of negative sorption of the salts dissolved in the lye or mother-liquor. The value $NaP,2{\cdot}1H_2O$ for the hydration of sodium palmitate in the presence of a nearly saturated solution of sodium chloride at 90° has been established by several methods. It has been shown that these fibres sorb small amounts of sodium chloride, and the same has been found to be true of sodium sulphate, except in the presence of a large amount of some other salt.

The present work was undertaken in the hope of finding some easily analysable reference substance which would be applicable in all cases to the determination of the hydration of soap fibres and incidentally to the extension of the existing scanty knowledge of the sorption of various substances by curd fibres.

Glycerol is the only one of the substances here investigated which is neither appreciably sorbed nor decomposed by the soap; it is not, however, easy to use as a reference substance. This result is of twofold interest. In the first place, the hydration value obtained with it, $NaP,2{\cdot}0H_2O$, agrees with the value obtained by the previous methods. In the second place, glycerol being a most important material from a commercial point of view, it becomes evident that the loss of the glycerol retained in the soap (equal, perhaps, to 10 per cent. of the world's output) is not inherently unavoidable, for all the glycerol may be washed out from the soap curd, being not chemically combined, but merely held in the mechanically entangled lye. The problem is that of washing a wet precipitate. The expense of recovering a large part of this glycerol is a commercial question, but it is possible to do it by a suitable modification of the process of soap-boiling.

EXPERIMENTAL.

Pure sodium palmitate was prepared as follows: Sodium wire which had been cleaned in methylated ether was dissolved in alcohol that had been distilled after standing for a year over calcium oxide and was therefore thoroughly dry. The sodium ethoxide formed was treated with palmitic acid (Kahlbaum) until the alcoholic soap solution, after dilution with a recently boiled mixture of alcohol and water (3 : 1), was found, by repeated tests, to give a neutral reaction with a neutral alcoholic solution of phenolphthalein. After being isolated, the sodium palmitate was dried for a week in a vacuum desiccator and was thus obtained as a pure white powder.

The dry, neutral sodium palmitate was weighed into a glass tube and dissolved in the necessary quantity of a solution of sodium chloride containing the reference substance to make the solution approximately normal with respect to sodium palmitate. Glass was not affected by sodium chloride, but it was not used with alkali, because in blank experiments the concentration of *N*/10-sodium hydroxide increased by 5 per cent. and of a 2·5*N*-solution by 11 per cent. after shaking at 90° during one week.

The glass tubes were sealed and shaken for one week at 90° and allowed to stand for another week at 90°. In this way a maximum amount of lye was obtained, as in some cases the separation of the two layers required several days and in others there was no appreciable separation after long periods at 90°. The tubes were opened and the lye was withdrawn with a pipette fitted with a glass filter-cap specially designed to filter all the solution through a single thickness of filter-paper about 1 mm. in diameter. The first few drops of lye were discarded in case the tiny piece of filter-paper had sorbed any of the reference substance. In all later analyses the water content of the lye was found by evaporation of samples, after a few drops of hydrochloric acid had been added to decompose any soap that might possibly have been present. All duplicate samples gave the same percentage loss of water.

In some cases the concentration of the reference substance was very low owing to the fact that some salts were salted out in concentrated sodium chloride solution, their solubility being lessened. In such cases the blank analyses (in duplicate) were alone taken to give the original concentration. In others the weighed amounts taken agreed with those analytically determined in blank experiments.

It should be clearly understood that the absence of glycerol from curd fibres which have been salted out at 90° has nothing at all to do with the phenomena evolved when "neat soap" is formed as an upper layer in soap-boiling. This neat soap containing 30 per cent. of water is not a curd, but it is a liquid, whether gel or sol, and the concentration of glycerol in this liquid is governed by the law of distribution between it and the lower layer, whether nigre or lye. These relationships will be dealt with in other communications from this laboratory.

The previous paragraph therefore refers only to curd in the presence of graining lyes.

All the chemicals employed, except sodium formate, were Kahlbaum's best. All vessels were carefully calibrated. Concentrations are expressed in weight normality, mols. per 1000 grams of water.

Analytical Methods.

It must always be remembered in evaluating these results that each case represents small differences between large numbers, hence any slight error in the analysis is considerably magnified (up to thirty-fold) in the sorption or hydration results deduced. When the quantity of lye obtained was larger, the results were more accurate, and thus agreed very closely in blank experiments, but duplicate estimations did not give very concordant values when, as in most cases, the quantity of lye was scarcely adequate.

The presence even of traces of an unsaturated acid or of an oxidisable impurity in the soap would prohibit the use of an oxidising material as reference substance.

In most cases, volumetric methods were employed in the preliminary experiments, but where a compound seemed to be a promising reference substance, gravimetric analysis was carried out also.

Glycerol was analysed by the acetin method with the following modifications. The sodium chloride solution or lye containing the glycerol was treated with sulphuric acid to decompose any soap present and the sulphuric acid removed by barium chloride. The ethereal extract of the dried barium residue was evaporated to dryness in a silica flask on a water-bath with the aid of a suction-pump. As any estimation in the presence of a slight trace of water or alcohol was valueless, the residue, before being analysed, was left over-night in a vacuum desiccator containing calcium chloride. The silica flask was fitted with a ground-in silica condenser. This arrangement greatly simplifies the procedure, for with continued boiling in glass the mixture of acetic anhydride and glycerol extract is liable to cake, causing fracture of the flask by local overheating. It also allows of rapid cooling of the contents of the flask.

Experimental Results.

Incidental observations were made on the characteristics of the soap curd, particularly as regards its hardness and the extent to which the lye was retained enmeshed in the curd on standing as well as after suction (Table I). For instance, the striking combination of effects produced by small quantities of phenol would be of practical importance were it not for the fact that they are observed only with chemically pure palmitate. Commercial palmitates do not show this behaviour, probably because the effect is, as other experiments show, in the opposite direction with unsaturated soaps such as the oleate. Sodium phenoxide greatly lowers the so-called melting point of curds of pure sodium oleate, an effect which is in the opposite direction to that observed with eight other salts investigated.

TABLE I.

Appearance of the curd and the lye when sodium palmitate is salted out by saturated sodium chloride solution in presence of small amounts of various substances.

Reference substance.	Clear lye visible.	Proportion of the lye finally recovered.*	Curd.
Sodium oxalate	None	$\frac{1}{4}$	—†
Potassium iodide	Scanty	$\frac{1}{10}$	Soft
,, bromate	Scanty	$\frac{1}{8}$	—
,, chromate	Scanty, pale yellow	$\frac{1}{3}$	Very yellow
Sodium formate	None	$\frac{1}{6}$	Hard
Acetone	Plenty	$\frac{1}{4}$	Very soft
Phenol	None	$\frac{1}{20}$	Very firm
Sodium thiosulphate	Very little	$\frac{1}{4}$	Soft
Glycerol	Scanty	$\frac{1}{3}$	—
Sodium hydroxide	Plenty	$\frac{1}{4}$	Soft

* See columns 5 and 6 in Tables II and III, which show approximately how much lye was mechanically retained in the curd after suction. The amount of lye obtained was, in most cases, greater than that recorded in column 5, the remainder having been used for the estimation of the water.

† The dash (—) indicates that the appearance and the hardness of the curd were not noticeably different from those of the curd obtained in the absence of the reference substance.

Table II contains the data for nine reference substances (for clearness, the weights are only recorded in rounded-off numbers).

Table III contains the data for the sorption of the reference substances of Table II. The calculation of these results involves the hydration value NaP,$2{\cdot}1H_2O$ previously established, which necessitates a correction of the percentage change in the concentration of the lye recorded in Table II in order to allow for the water abstracted to form the fibres. The true sorption of the reference substance is expressed in three different ways: first, in

TABLE II.

Concentration changes in the added reference substance when sodium palmitate is salted out at 90°.

Reference substance.	Normality of NaP.	Weight normality of reference substance.	Grams used.		Lye obtained.		Percentage change in concentration of reference substance in the lye.
			NaP.	Lye.	Grams.	Normality.	
Sodium oxalate	1·0	0·003	5	16	3·8	0·00295	– 17·2
Potassium iodide	1·23	0·080	5	20	1·4	0·069	– 13·4
	1·23	0·815	5	20	1·6	0·072	– 11·5
	0·98	0·080	3	15	2·2	0·071	– 11·3
					1·9	0·070	– 11·7
„ bromate	1·50	0·0296	5	16	1·9	—	—
„ chromate	1·50	0·0254	5	16	5	0·0089	– 65·0?
Sodium formate	1·23	0·1962	5	20	4·3	*	*
					2·6		
Acetone	0·62	0·1205	3	24	4·8	0·0999	– 17·0
					2·0	0·995	– 17·4
Sodium thiosulphate	1·29	0·0649	5	19	4·1	0·064	– 1·5
					3·6	0·062	– 4·6
Phenol	1·25	0·0851	5	19·5	0·40	0·069	– 23
					0·85	0·074	– 16
	0·998	0·0557	4	19·5	2·6	0·040	– 28
Glycerol	1·10	0·1018	4	17	6·6	0·1059	– 3·6
	0·52	0·1021	3	18	6·8	0·1053	– 3·2

* The trace of soap in the lye was sufficient to vitiate the analyses, probably during the boiling with alkali and permanganate.

the percentage of the total reference substance present which has been sorbed by the curd fibres; secondly, in the percentage by weight, that is, the weight in grams sorbed by 100 grams of NaP,$2{\cdot}1H_2O$; thirdly, in order to render the results roughly comparable, in mols. of reference substance sorbed by 1 mol. of sodium palmitate—for an accurate comparison the sorption law would have to be determined for each case.

It should be noted that whereas there is a real positive sorption of the reference substance in each case except glycerol, nevertheless the greater part of the reference substance is left in the lye, and that it forms only an inconsiderable percentage of the weight of the curd fibres themselves.

Other glycerol results, which are not quoted in the tables owing to the inadequate quantities of lye available, always showed a similar increase in concentration of glycerol, in agreement with the view that it is not sorbed by curd fibres.

TABLE III.

Sorption of various substances by sodium palmitate at 90° in presence of saturated sodium chloride solution.

Reference substance.	Grams of reference substance per 100 grams of water.	Mols. of NaP.	Fate of reference substance.	True sorption of reference substance.		
				Proportion per cent.	Percentage by weight of soap.	Mols. sorbed per 1 mol. of NaP.
Sodium oxalate	0·046	1·0	sorbed	22·63	0·042	0·00087
Potassium iodide	1·322	1·23	,,	17·2	0·695	0·012
	1·325	1·23	,,	16·1	0·639	0·011
	1·173	0·98	,,	11·6	0·561	0·009
	1·168	0·98	,,	11·9	0·580	0·010
,, bromate	0·494	1·50	reduced	bromide only present		
,, chromate	0·493	1·50	,,	66·8	0·830	0·012
Acetone	0·726	0·615	sorbed	19·0	0·797	0·038
	0·726	0·615	,,	19·4	0·811	0·039
Sodium thiosulphate	0·672	1·29	,,	5·95	0·177	0·003
	0·672	,,	,,	9·02	0·177	0·005
Phenol	0·800	1·25	,,	21·7	0·401	0·015
	0·800	,,	,,	11·4	0·303	0·012
	0·524	0·998	,,	30·8	0·600	0·018
Glycerol	0·94	1·10	unchanged			
	0·94	0·82	,,			

Sorption of Sodium Hydroxide.

There is an inherent difficulty in experimenting with sodium hydroxide in that it is one of the constituents of the soap itself, and it is difficult to be quite sure, first, that the reaction between sodium hydroxide and palmitic acid is completed, because of the salting-out action of saturated sodium chloride solution, and, secondly, that the actual hydrolysis of the soap itself has not been altered in the process of salting-out.

The concentrations taken were very low, since for solutions between 1·5*N* and 3·0*N* conclusive work had already been carried out (Part I, *loc. cit.*). In that work, repeated experiments showed that concentrated solutions increase in concentration owing to removal of water for the hydration of the curd.

The results in Table IV were obtained by experiments carried out in sealed silver tubes. The solution of sodium palmitate was made up in two ways, namely, in that already recorded and by mixing the requisite quantities of palmitic acid and solution of sodium hydroxide. The last six lines of the table refer to solutions of sodium hydroxide which had been directly standardised against the pure palmitic acid used, to ensure that the alterations of concentration of sodium hydroxide were not due to relatively slight inaccuracy in making up the comparatively large amounts of sodium palmitate. In all the latter cases, pure ignited sodium chloride in solid form was added to the original charge.

TABLE IV.

Sorption of dilute sodium hydroxide by curd fibres of sodium palmitate salted out at 90° by nearly saturated sodium chloride solution.

Preparation.	Weight normality of soap.	Weight normality of excess of NaOH. Before.	After.	Sorption. Apparent per cent. change.	Mols. of NaOH per 1 mol. of NaP.
NaP + brine + excess of NaOH	1·00	0·1163	(*a*) 0·1029 * (*b*) 0·1062	9·5	0·012
	1·045	0·1571	(*a*) 0·1409 (*b*) 0·1428	9·4	0·015
	0·99	0·0993	(*a*) 0·08136 (*b*) 0·08140	18·1	0·018
NaOH	0·9618	0·0944	(*a*) 0·08242 (*b*) 0·08180	13·4	0·012
	1·00	0·2006	(*a*) 0·0719	14·3	0·29
† Standardised HP + NaOH + solid sodium chloride	1·00	0·2081	(*a*) 0·1856 (*b*) 0·1869	10·5	0·022
	0·9863	0·1120	(*a*) 0·0820 (*b*) 0·0768	29·0	0·033
	0·9868	0·1163	(*a*) 0·08275 (*b*) 0·08433	28·2	0·033

* (*a*)—(*b*) refer to experiments in two separate silver tubes, each determined in duplicate.

† In the last series, repeated some months after the first two, the palmitic acid was standardised against the sodium hydroxide employed.

The results show conclusively that there is a real positive sorption of sodium hydroxide from dilute solutions. For 0·1*N*-sodium hydroxide this amounts to between 10—29 (weighted mean 22 per cent.), and for 0·2*N*-sodium hydroxide, 10—14 (weighted mean 11 per cent.). The corresponding empirical formula for the curd fibres in both cases is $NaP,2{\cdot}1H_2O,0{\cdot}022NaOH$.

Although it is improbable that the sorption of sodium hydroxide does not increase at all with concentration, yet the data strongly indicate that this is approximately the case. This is in accordance with results obtained in Part I with concentrated solutions, where pronounced negative sorption was actually observed, so that the amount of water taken up wholly masked the slight amount of sorbed sodium hydroxide. The effect of this would be to bear out what has been emphasised in Parts I and II. The method of negative sorption yields minimum values, which could be increased, for example, in the case of 3·0*N*-sodium hydroxide, by about 0·4 mol. of water giving a result of, say, $NaP,3{\cdot}6H_2O$ in place of $NaP,3{\cdot}2H_2O$.

In connexion with other work, it is important to note that the presence of *N*/10-sodium hydroxide has now been proved, not only to eliminate hydrolysis completely, but even to render the curd fibres very slightly alkaline when salted out with concentrated sodium chloride solution.

Summary.

The sorption of widely different substances by soap curd has been investigated for the first time.

When 1 mol. of sodium palmitate is treated with brine containing about 1000 grams of water, 330 grams of sodium chloride, and 5—10 grams of the substance under investigation, an appreciable fraction ($\frac{1}{16}$ to $\frac{1}{3}$) of the following are sorbed by the soap curd; acetone, phenol, potassium chromate and iodide, sodium acetate, thiosulphate, and hydroxide.

Sodium sulphate and glycerol are quantitatively left in the lye; their apparent presence in soap curd is due only to the enmeshed lye. This solves an old and important problem as to the form in which glycerol is present in soaps.

Under the above conditions (salting out with saturated sodium chloride solution), in confirmation of previous work from this laboratory, the hydration of the solid part of wet soap curd amounts to $1NaP,2H_2O$.

Sodium hydroxide is sorbed by curd fibres to an extent probably not exceeding about 0·02 equivalents of sodium hydroxide to 1 equivalent of sodium palmitate.

In conclusion, I wish to thank the Colston Research Society of the University of Bristol and the Chemical Society for grants for the purchase of pure materials, which enabled this investigation to be carried out.

CHEMICAL DEPARTMENT,
BRISTOL UNIVERSITY.

[*Received, July* 30*th,* 1921.]

CXC.—*The Propagation of Flame in Mixtures of Ethylene and Air.*

By William Ronald Chapman.

The " uniform movement " of flame, which occurs when an inflammable mixture contained in a tube closed at one end is ignited at the open end, affords means of comparison between one inflammable gas and another as regards their general behaviour on burning. The speed of the uniform movement is dependent on the character of the combustible gas and the composition of the mixture that is inflamed, but it is also dependent on the experimental conditions, notably on the diameter of the tube in which the mixture is contained. When desirous of comparing one mixture with another, or a series of mixtures of one inflammable gas and air with that of another inflammable gas, it is essential, therefore, that the records of speeds employed should have been obtained under standard conditions.

Records of the speed of the uniform movement of flame in all their mixtures with air over the range of inflammability are available for most of the common inflammable gases, as determined in horizontal glass tubes 2·5 cm. in diameter. Thus, for hydrogen reference can be made to Haward and Otagawa (T., 1916, **109**, 83), for methane and acetylene to Mason and Wheeler (T., 1917, **111**, 1044; 1919, **115**, 578), and for ethane and the higher paraffins, and for carbon monoxide, to Payman (T., 1919, **115**, 1446, 1454). For ethylene information has not hitherto been available and, since ethylene is an important constituent of coal-gas, it is desirable that it should be.

The present paper records for ethylene (1) its limits of inflammability, and (2) the speed of the uniform movement of flame in all its mixtures with air, as determined in a glass tube 2·5 cm. in diameter.

Limits of Inflammability.

The results obtained are given in the table that follows. With tubes of larger diameter the limits would, no doubt, be slightly wider (in this connexion see T., 1918, **113**, 656).

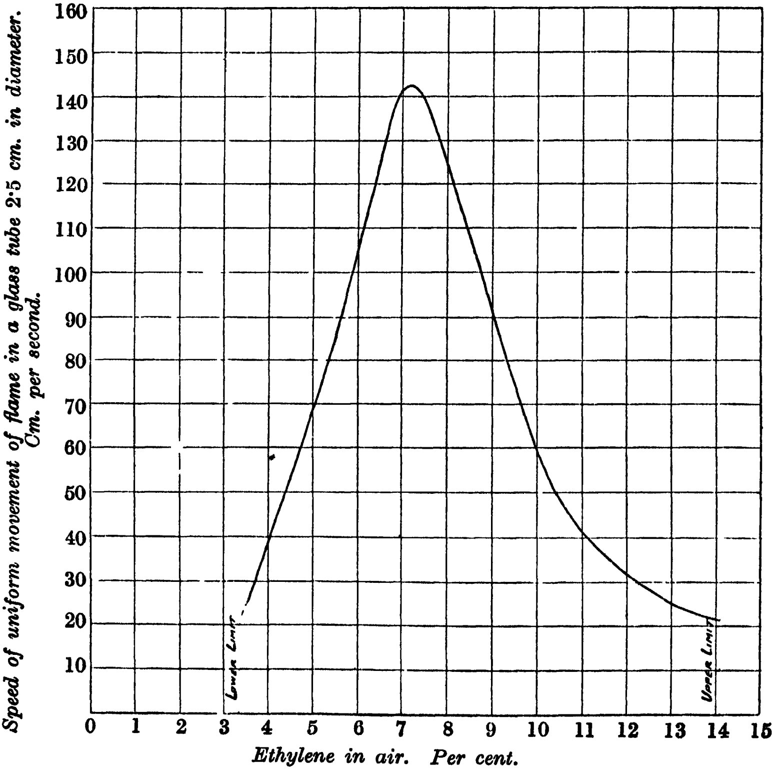
	Ethylene per cent.	Remarks.
Horizontal propagation.		
Lower limit	3·4	A pale blue flame occupied the upper portion of the tube only. The upper limit flame was tinged with yellow.
Upper limit	14·1	

	Ethylene per cent.	Remarks.
Vertical propagation, downward.		
Lower limit	3·6	Pale blue disc.
Upper limit	13·7	Pale blue, voluminous flame.
Vertical propagation, upward.		
Lower limit	3·3	Blue flare of flame.
Upper limit	25·6	Smoky, yellow flame, carbon deposited on sides of tube.

Speed of Propagation of Flame.

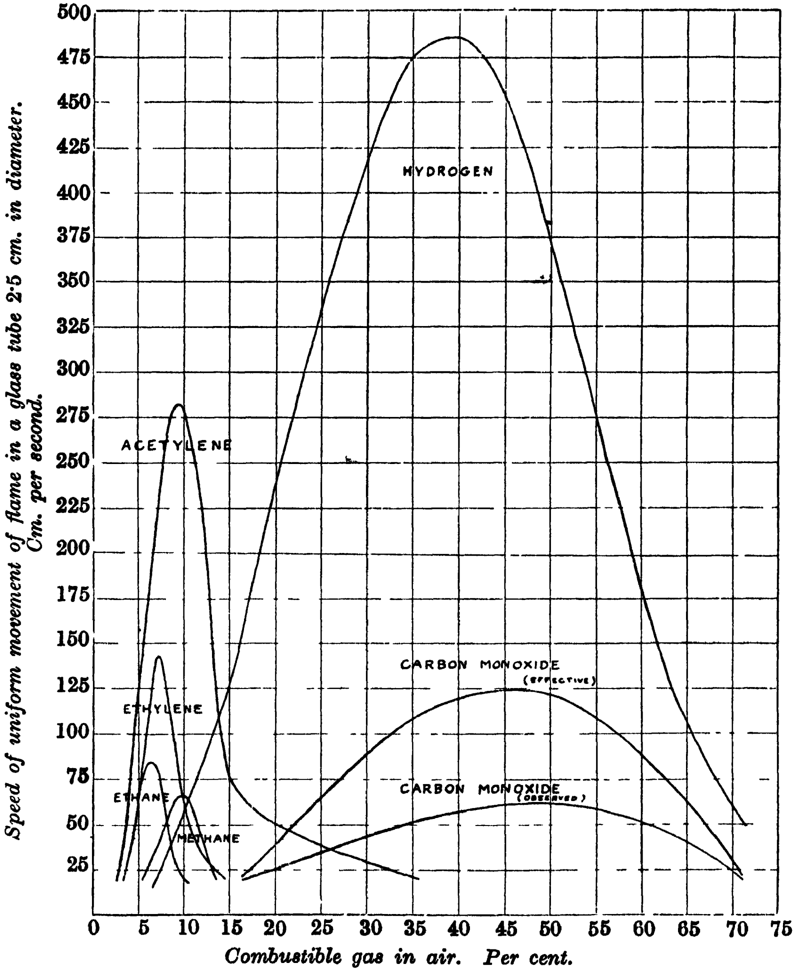
The measurements of the speed of the uniform movement are most conveniently displayed in diagrammatic form (Fig. 1). The

FIG. 1.



curve relating speeds with percentages of ethylene is of a form similar to that obtained with other hydrocarbons; that is to say, the speed of the flame increases rapidly as the percentage of ethylene is increased from that in the lower-limit mixture until a maximum range is reached, after which it decreases. As with each of the paraffin hydrocarbons under the same conditions of experiment, the speed of the flame at the limits tends towards a value of 20 cm. per second, which would therefore appear to be a constant for the hydrocarbons.*

Fig. 2.



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* With mixtures of carbon monoxide and air the speed of flame at the limits (under the same conditions of experiment) is also about 20 cm. per second; whereas with the lower-limit mixture of hydrogen and air the speed is abnormally slow, namely, 10 cm. per second (see T., 1919, **115**, 1444).

In Fig. 2 the speed–percentage curves for the uniform movement of flame in mixtures of air with hydrogen, carbon monoxide (the "effective" values and those "observed" when saturated with water-vapour at 12° and 750 mm.), methane, ethane, acetylene, and ethylene respectively, as determined in horizontal glass tubes 2·5 cm. in diameter, are plotted to the same scale for comparison. The curve for ethylene is intermediate in character between those for methane and acetylene, not only as regards its maximum range, but also in respect of the manner in which it flattens as the upper limit is approached. This flattening of the curve towards the upper limit is just noticeable with methane (it becomes more pronounced when tubes of larger diameter than 2·5 cm. are employed), is quite distinct with ethylene, and is very marked with acetylene, where it is due to exothermic decomposition of excess of the gas (see T., 1919, **115**, 578). With ethylene, as with the paraffin hydrocarbons, the flattening of the curve as the excess of combustible gas becomes greater is probably due to the liberation of hydrogen at an intermediate stage in the combustion of the hydrocarbon.

The mixture of ethylene and air that contains ethylene and oxygen in combining proportions to form carbon dioxide and steam contains 6·5 per cent. of ethylene, and this mixture has the maximum calorific effect. The maximum speed of uniform movement of flame is, however, obtained with mixtures containing between 7 and 7·25 per cent. of ethylene. This " displacement " of the maximum-speed mixture, which has been observed to a greater or less extent with all mixtures of inflammable gases with air, has been shown by Payman to be an effect of mass action (T., 1920, **117**, 48).

Given data respecting the compositions of the maximum-speed mixtures with air of individual combustible gases, and the speeds of flame in them, it is possible to calculate the maximum-speed mixture, and the speed obtainable, when a composite gas, such as coal-gas, containing the individuals in known proportions, is mixed with air. Taking as an example a coal-gas containing, per cent.

Carbon dioxide	2·6
Ethylene	3·0
Carbon monoxide	14·1
Hydrogen	46·9
Methane	19·0
Ethane	4·5
Nitrogen	9·9

the composition of the maximum-speed mixture can be calculated by means of the formula

$$M = 100/\left\{\frac{a}{M_a} + \frac{b}{M_b} + \frac{c}{M_c} + \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot\right\}$$

in which a, b, c, . . . are the percentages of the individual gases in the coal-gas, and M_a, M_b, M_c, . . . the percentages in their respective maximum-speed mixtures with air. The result of the calculation is 22·2, meaning that the maximum speed of uniform movement of flame in a tube 2·5 cm. in diameter is obtained when 22·2 per cent. of the coal-gas is present in the mixture with air.

The value of the speed of flame in this mixture can be calculated from the formula

$$S = \frac{lS_l + mS_m + nS_n + \ldots\ldots}{l + m + n +}$$

in which l, m, n, . . . are the amounts present of the maximum-speed mixture with air of each constituent gas, and S_l, S_m, S_n . . . are the speeds of flame in those mixtures. In the instance given, the calculated speed (using the "effective" value for carbon monoxide) is 210·5 cm. per second.

So far as calculations for different compositions of coal-gas are concerned, a sufficiently close approximation can be obtained by grouping together the paraffins and olefines and treating them as though they were methane. Thus, for the sample of coal-gas taken as an illustration, the maximum-speed mixture calculated on this assumption contains 22·7 per cent. of coal-gas and the speed of flame in that mixture is 206·2 cm. per second.

This research has been extended to include the study of the propagation of flame in mixtures of the higher members of the olefine series of hydrocarbons with air. For propylene, for example, the limits of inflammability (horizontal propagation of flame) are 2·6 and 7·4, and the maximum speed of the uniform movement, under the same conditions of experiment as for ethylene, is 90 cm. per second, obtained with mixtures containing between 4·8 and 5·3 per cent. of propylene. The significance of a comparison between the values obtained for ethylene, propylene, and butylene on the one hand and ethane, propane, and butane on the other will be discussed in a future communication. For the present it may be mentioned that the higher olefines correspond more closely to the paraffins than does ethylene, so far as the speed of uniform movement of flame in their mixtures with air is concerned. Coal-gas contains, in addition to ethylene, appreciable quantities of propylene and butylene, which are usually recorded in analyses as ethylene (or as "olefines"), so that the grouping together of paraffins and olefines when making such calculations as are described above would, in the majority of instances, cause even less departure from an exact calculation than appears in the illustration that is given.

EXPERIMENTAL.

Ethylene was prepared by the dehydration of absolute ethyl alcohol by phosphoric acid at 200—220° (Newth, T., 1901, **79**, 901) and purified by passing through a condenser cooled by solid carbon dioxide. Explosion analysis gave a ratio *C*/*A* of 1·00, showing a high degree of purity. The mixtures with air were prepared over glycerol and water in glass gas-holders and were analysed before use.

The determinations of the limits of inflammability were made in a glass tube 2·5 cm. in diameter and 150 cm. long. The measurements of speeds of flame were made by the " screen-wire " method described by Wheeler (T., 1914, **105**, 2609), a glass tube 2·5 cm. in diameter and 300 cm. long being employed. Three screen-wires were used 25 cm. apart, the first being 20 cm. from the point of ignition. These wires were supported on platinum leads which passed through ground-glass stoppers fitted into tubulures. The tube, which had a tap fused on at one end and could be temporarily closed at the other end by a ground-glass cover, was exhausted of air before each experiment, filled with the required mixture from the gas-holder, re-exhausted and filled again. Ignition in the majority of the experiments was by means of an electric spark at platinum electrodes fused through the walls of the tube 2 cm. from the open end; in the remaining experiments a lighted taper was passed across the mouth of the tube.

The flames were of a pale blue colour tinged with pink. They usually travelled at a uniform speed over a distance of about 90 cm. from the point of ignition; occasionally, with the fastest flames, the " vibratory movement " began before the third screen-wire was reached (70 cm. from the point of ignition), when the measurements of speed between the first and second screen-wires only were recorded. Details of the results are as follow :

Ethylene per cent.	Speed in cm. per sec.	Ethylene per cent.	Speed in cm. per sec.
3·55	25·8	7·20	142·4
3·60	29·4	7·40	139·7
3·80	36·8	7·70	127·5
4·00	41·3	8·10	120·6
4·70	57·9	8·45	113·7
5·40	79·4	8·65	113·4
6·10	108·4	9·00	89·5
6·40	121·6	9·45	72·6
6·45	129·3	10·65	45·5
6·50	129·9	13·35	23·5
6·60	133·5	13·80	22·3
6·90	140·2	14·00	22·2

This work, in which I have been assisted by Mr. C. A. Naylor, has been carried out at the Mines Department Experimental Station, Eskmeals, under the direction of Dr. R. V. Wheeler.

DEPARTMENT OF FUEL TECHNOLOGY,
THE UNIVERSITY, SHEFFIELD. [*Received, September 12th, 1921.*]

CXCI.—*The Effect of Temperature on Platinum Black and other Finely-Divided Metals.*

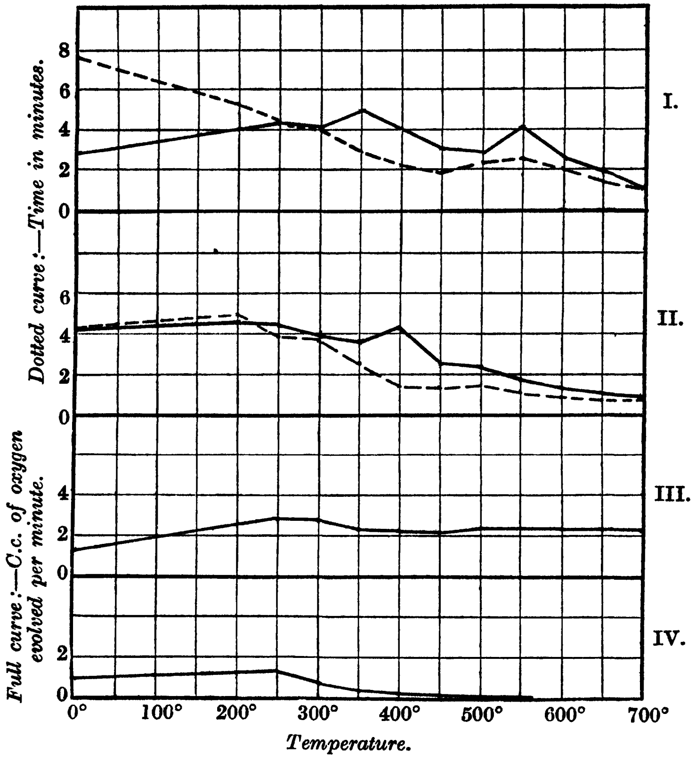
By ROBERT WRIGHT and ROBERT CHRISTIE SMITH.

WHEN a freshly-coated platinum plate has been heated to a temperature somewhat above red heat and allowed to cool, the original velvet-black surface becomes grey, the extent of the colour lightening depending on the temperature and the duration of the heating.

This change in platinum black is not attended by any alteration in weight, and cannot therefore be due to oxidation or to the removal of the deposited surface. Moreover, the change does not take place at any definite temperature, as a plate heated in a resistance furnace and examined at every 50° began to show the change at 300°, the effect increasing with rise of temperature until, at 900°, the deposit had become almost white.

In order to determine whether the heating produced any other change in the platinum black beyond the alteration of colour, several properties of the metal were examined, measurements being made immediately after the deposition of a fresh coat and also after heating the coated plate to a series of definite temperatures. The properties which gave most satisfactory results were the decomposition of hydrogen peroxide by the finely-divided metal and the absorptive capacity of the plates for hydrogen and oxygen when the plates were used as electrodes in a storage cell charged with dilute sulphuric acid. The alteration of the overvoltage shown by the plates in dilute acid was also examined, but no definite results were obtained, although both the anodic and the cathodic decomposition potentials with polished platinum differ considerably from those shown by platinised electrodes.

The results of the hydrogen peroxide decompositions and the storage capacities of the plates as electrodes are shown in the set of curves. The first two sets were obtained with platinum, the third with silver, and the last with palladium. In all cases the abscissæ represent the temperatures to which the plates were heated, and the ordinates correspond either with cubic centimetres of oxygen evolved per minute, or with the time in minutes taken for the storage cell, constructed of the given plates in dilute sulphuric acid, to fall to a potential of 0·4 volt when discharged through a fixed external resistance. The full-line curves represent the results of the peroxide decompositions, and the dotted curves the results for cell capacity. The capacity measurements were satisfactory only in the case of platinum, as palladium absorbs an excessive quantity of hydrogen, whilst silver unites with the radicle of the acid used.



I. *Platinum.* II. *Platinum free from chlorine.*
III. *Silver.* IV. *Palladium.*

The first set of curves for platinum was obtained by using plates platinised in the ordinary way, that is, by reversing the current every half minute during the deposition of the platinum black. It was thought that such plates might contain considerable quantities of chlorine, so a second set of measurements was carried out in which the current was not reversed during the plating and the cathode was kept in a separate vessel from the anode, the two being connected by means of a syphon. By this method, not only is no chlorine evolved at the cathode, but also the possible diffusion of chlorine from the anode is practically prevented. It will be seen from the curves that the catalytic action of the chlorine-free plate is not augmented to the same extent by low temperature as is the case with the plate which possibly contained occluded chlorine. Further evidence of the presence of chlorine in the plate was obtained by plating with reversal of current and then—after washing—by heating the plate in a closed vessel through which a current of air was drawn, the air being afterwards passed through a starch-iodide solution. Under these conditions the starch gave a blue colour, due to the liberation of iodine by the chlorine, but when the platinum was deposited free from chlorine in the manner indicated, no blue colour was obtained.

Considering the catalytic action of the metals as shown by the full-line curves, two points should be noted; first, the temporary increase in activity which occurs after heating to certain temperatures, and secondly, the gradual falling off in activity as high temperatures are reached. The first effect may be explained by the evolution of occluded gas, the escape of which would not only increase the roughness of the plates, but also, in some cases, help the catalysis by the removal of a catalytic poison. The falling off in catalytic power which takes place when high temperatures are reached is probably due to a decrease in the specific surface of the deposited metal, accompanied by an alteration in the size and number of points at which the liberated oxygen can escape in the form of bubbles. The storage capacity of the plates when used as electrodes in a storage cell also falls off, after heating, in the manner shown by the dotted curves in the first two figures. In this case also the same explanation will hold good, that is, the decrease in specific surface produced by heating will be accompanied by a falling off in the occlusive power of the plates for gases, and therefore also in their storage capacity when used as electrodes in a storage cell.

If the view of the decrease of specific surface be accepted, then it should be possible to detect such an alteration by application of the microscope. Photomicrographs of the plates, made before and after heating, were unsatisfactory owing to the lack of contrast between the different parts of the plated surface. The plan was therefore adopted of photographing a plated wire against a bright background, so that in effect a silhouette of the plated wire was obtained; the wire was then heated, usually by an electric current, and then rephotographed. Wires of platinum, silver, iron, and copper were examined in this manner; with the exception of platinum, the wires were heated in an atmosphere of hydrogen to avoid oxidation. Substances of low melting point were not investigated owing to the difficulty of judging the temperature when heating by the current, that is, in all cases the melting point of the wire was considerably above red heat. The results obtained are shown in the table. The figures given are proportional to the diameters of the plated wires before and after heating, the diameter of the unplated wire being taken as unity in each case. In all cases a portion of the plating was removed from the freshly-coated wire, so that the original diameter was always shown in the photographs, thus providing a standard and avoiding errors of focus. The results clearly indicate that heating is in all cases followed by a decrease of specific surface.

	Diameter before heating.	Diameter after heating to dull redness.
Platinum	1·31	1·15
Silver	1·21	1·11
Iron	2·00	1·41
Copper	1·66	1·36

Faraday (*Phil. Trans.*, 1857, **147**, 145) observed that a gold leaf mounted on glass and heated to about 500° lost its green colour when viewed by transmitted light and became transparent, the green colour being restored on burnishing. Turner (*Proc. Roy. Soc.*, 1908, [*A*], **81**, 301) repeated the experiment and took photomicrographs of the transparent gold. By this means he showed that the film had ceased to be continuous and had gathered itself up into a network of gold strands, the effect of burnishing being to flatten out the strands again so as to reproduce the original surface. Beilby (*Proc. Roy. Soc.*, 1904, **72**, 226), and Chapman and Porter (*ibid.*, 1910, [*A*], **83**, 65) investigated the same phenomenon and advanced the view that the effect was produced by the surface tension of the metal, which was able to operate owing to the lower rigidity produced by heating. Chapman and Porter also showed that a freely-suspended leaf merely contracts in area but remains continuous on heating, the network effect only being produced when the leaf was mounted on glass. With the thickness of leaf they employed, the contraction started at the definite temperature of 340°.

A different explanation of the observed effects also seems possible. A very finely-divided metal may have a considerably lower melting point than the same substance in bulk, and as a result of this incipient melting the smaller particles would attach themselves to the larger, which would not only grow, but would also become cemented together by the liquid smaller particles, the whole effect corresponding with a low-temperature sintering of the finely-divided metal. The increased vapour pressure of a finely-divided liquid in the state of mist, where the large drops grow at the expense of the smaller, and the increased solubility obtained by using a substance in a fine state of division, are corresponding phenomena. Therefore it may be assumed that fine division alters the melting point as well as the vapour pressure and the solubility. Whatever the cause may be, there seems little doubt that finely-divided metals show a very considerable decrease of specific surface when heated to temperatures much below their usual melting points.

Further evidence in support of the theory can be deduced from the fact that finely-divided metals, when used as catalysts, are always more active when produced by reduction at low temperatures, the same being true in connexion with the activity of the metallic pyrophori made from nickel or iron. In both cases the metal produced at a low temperature has a high specific surface, which is considerably reduced by the particles melting together at higher temperatures. It should be noted that the sintering effect may be to some extent prevented if the catalytic metal is mounted on a carrier such as asbestos, for under such conditions the metallic particles are to a certain extent kept separate from each other. It is also interesting to note that, as a rule, surface catalysts are substances of very high melting point, and that the optimum temperature for any given catalyst is always considerably below its melting point.

EXPERIMENTAL.

The plates used measured 25 by 35 mm. and were fitted with wires of the same metal welded on to them. The electrolysing solutions were chlorides in the case of palladium and platinum, cyanide in that of silver, and sulphates in the cases of copper and iron. After deposition of the metal, the surface was cleaned by using the plates as electrodes in a solution of dilute sulphuric acid; the plates were then washed in distilled water and dried. The heating of the plates was carried out in a small resistance furnace, the temperature being noted by means of a thermo-couple.

The storage cell was filled with *N*-sulphuric acid, and the plates were charged by connecting them with a 2-volt accumulator for fifteen seconds; the current was then broken and the cell allowed to discharge itself through a voltmeter of 390 ohms resistance and graduated to 1/100th of a volt. The time required for the cell voltage to fall to 0·4 volt was taken as an indication of the storage capacity of the plates.

Before the plates were used for the decomposition of hydrogen peroxide, the platinum and palladium plates were saturated with oxygen, and the silver with hydrogen, by using them as electrodes in a cell filled with dilute sulphuric acid. The peroxide used was of approximately two-volume strength, and the same solution was always employed for any series of measurements, the strength being checked from time to time by titration with potassium permanganate. Twenty-five c.c. of the solution were placed in a wide test-tube, and allowed to stand in a bath until it attained a temperature of 18°; the electrode was then introduced and the tube was closed by a rubber stopper connected with a three-way tap open to the air. Fifteen seconds after the introduction of the electrode, the tap was turned so as to make connexion between the test-tube and a Hempel gas-burette. The quantity of oxygen evolved per minute was noted, the figure plotted being the mean value obtained during the first three minutes.

The wires used in obtaining the photomicrographs were plated in the same way as the plates; the diameter varied between 0·15 and 0·3 mm. The platinum wire was merely held between terminals fitted into the edge of a slip of wood mounted on the microscope stage. A slip of paper was placed beneath the wire and illuminated from below so as to form a bright background, against which the wire was silhouetted. The heating was carried out by means of the electric current, no attempt being made to measure the temperature, but, judging by the colour of the glow, it always lay between 650° and 850°. The copper, silver, and iron wires were all mounted—after plating—between two steel wires passed through a rubber stopper. During heating, the stopper carrying the wires was used to close an inverted bottle, through which a stream of purified dry hydrogen was passed, the heated wire being in all cases allowed to cool in the atmosphere of hydrogen. After heating, the rubber stopper was removed from the bottle, mounted on the stage, and the wire photographed.

Conclusion.

The metals, silver, copper, iron, platinum, and palladium, when deposited electrolytically in a fine state of division, show the phenomenon of sintering at temperatures considerably below their ordinary melting points. It is thought that this effect may be parallel to the abnormal vapour pressure and solubility of finely-divided material. The effect probably has considerable influence on the optimum temperature of a finely-divided metal when used as a catalyst.

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[*Received, July 5th,* 1921.]

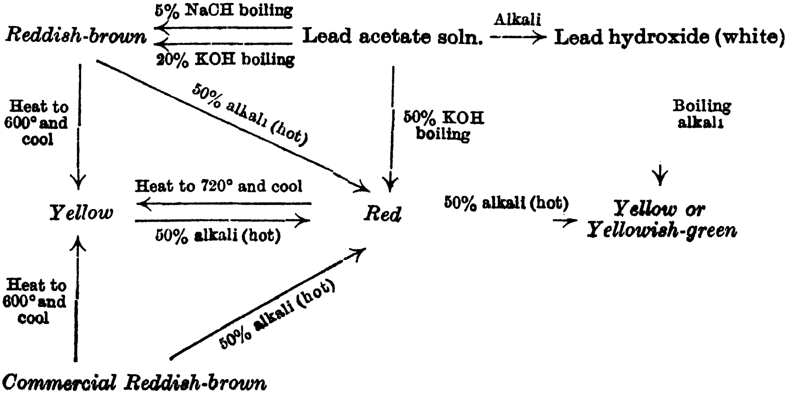
CXCII.—*Physical Chemistry of the Oxides of Lead. Part I. The Solubility of Lead Monoxide.*

By Samuel Glasstone.

This series of studies was originally undertaken with the object of investigating the affinity relationships between the various oxides of lead by electrochemical and other methods. It was found necessary to investigate the subject of lead monoxide in detail, owing to its existence in several coloured modifications. The first part of this work, consisting mainly of solubility determinations, is now described.

Red and yellow forms of lead monoxide were prepared by Geuther (*Annalen*, 1883, **219**, 56) by the action of alkalis on solutions of lead salts; in addition, it was found that a reddish-brown form, similar in colour to commercial litharge, could be prepared from these reagents. When a boiling 15 per cent. (or more dilute) solution of lead acetate is added to a boiling 5 per cent. (or more dilute) solution of sodium hydroxide, this reddish-brown form is directly precipitated. With potassium hydroxide (compare Winkelblech, *Annalen*, 1837, **21**, 21), provided both solutions are boiling, the formation of the reddish-brown oxide is independent of the concentration; the colour, however, becomes more and more red until, when a 50—60 per cent. solution of potassium hydroxide is used, it is identical with that of Geuther's red oxide. The reddish-brown form is thus probably the finely divided red modification.

The relationships between the various forms of lead monoxide may be set out as follows:



The facts that any form of lead monoxide, when heated with concentrated alkali hydroxide (50 per cent. or more), gives the red form, and that all forms on grinding give a brownish-yellow powder, suggested the possibility of a closer relationship between the forms of lead monoxide than that of allotropy, as worked out by Ruer (*Zeitsch. anorg. Chem.*, 1906, **50**, 265).

Preparation of Forms of Lead Monoxide.

The products were in each case washed with boiling water by decantation to remove the finer particles, then transferred to a Buchner funnel, well washed, and finally dried in a vacuum over calcium chloride.

No. 1. *Reddish-brown.*—A solution of 20 grams of sodium hydroxide in 400 c.c. of water was heated to the boiling point and treated gradually with a boiling solution of 60 grams of lead acetate in 400 c.c. of water.

No. 2. *Yellowish-green.*—To a solution of 30 grams of sodium hydroxide in 200 c.c. of water at 90° was slowly added a solution of 35 grams of lead acetate in 150 c.c. of water. The mixture was boiled until all the hydroxide had changed to a heavy, greenish-yellow solid, which settled to the bottom of the reaction vessel (a porcelain basin).

No. 3. *Red.*—120 Grams of sodium hydroxide dissolved in 180 c.c. of hot water were treated with a hot solution of 100 grams of lead acetate in 150 c.c. of water. The mixture was boiled for about an hour and stirred very frequently, small amounts of water being added to make up for the loss by evaporation. The yellow solid was completely converted into the red form.

No. 4. *Reddish-brown (prepared by means of potassium hydroxide).*—The quantities recorded in No. 2 were employed, but potassium hydroxide replaced sodium hydroxide, and both solutions were boiling while being mixed.

No. 5. *Yellowish-green (prepared by means of potassium hydroxide).*—The quantities used were exactly as in No. 4; the solutions, however, were mixed at a temperature below the boiling point and then boiled as in No. 2.

No. 6. *Lemon-yellow.*—Obtained by heating any of the other forms to 700° and allowing to cool (Ruer, *loc. cit.*).

No. 7. *Pure commercial lead monoxide.*—Reddish-brown flakes.

No. 8. *Brownish-yellow powder* made by grinding the red form No. 3 (compare Geuther, *loc. cit.*).

These specimens were all analysed, the lead being estimated gravimetrically as the sulphate. The percentage of lead found varied from 92·62 to 92·83 (PbO requires Pb = 92·83 per cent.); traces of moisture accounted for the low results.

Microscopic Examination.

The red form (No. 3) consisted of the largest particles, mainly 3μ to 5μ, which, on being heated to 700° and then cooled (No. 6), gave larger, yellow agglomerates (10μ to 20μ); the latter easily broke down under gentle pressure into particles smaller than those of the original red form (0·7μ to 1·5μ). Products No. 2 and No. 5 were similar to No. 6. The reddish-brown oxides (Nos. 1, 4, 7) consisted of particles smaller than those of the red form (1μ to 2μ), but of the same order as the finer particles of the yellow forms. It is believed that the particles into which the yellow agglomerates easily disrupt are also reddish-brown in colour, for the yellow form, when gently pressed on paper or in the mortar, gives a brown powder. The brown powder obtained by grinding any form of lead monoxide consisted almost uniformly of particles 0·7μ in diameter. All the specimens may possibly have contained particles smaller than 0·7μ which were not visible under the microscope. That such small particles are present is shown by the fact that freshly-prepared suspensions of lead monoxide in dilute alkali hydroxide solution often cannot be clarified by filtration through paper.

In accordance with the work of Ostwald (*Zeitsch. physikal. Chem.*, 1900, **34**, 495) and others, we should expect to find differences in solubility between the various forms of lead monoxide depending on the size of the particles. The red form should have the lowest solubility, and the reddish-brown forms higher values. The case of the yellow and yellowish-green forms is more uncertain. If the effect of shaking with a solvent is to break up the agglomerates (compare Hulett and Allen, *J. Amer. Chem. Soc.*, 1902, **24**, 667), these forms should have a solubility almost the same as that of the reddish-brown form; gentle stirring of the solvent over the surface of the solid would probably give lower values.

Solubility Determinations.

The solvent chosen was a *N*-solution of sodium hydroxide (free from carbonate), which was made by decomposing with water sodium amalgam that had been prepared by the electrolytic method (compare Ming Chow, *J. Amer. Chem. Soc.*, 1920, **42**, 488).

About 5 grams of lead oxide were shaken, (*a*) gently, in glass vessels tied to the spokes of a wheel which revolved at 24 revs.

per minute, and (*b*) vigorously, in bottles placed in a motor-driven shaking-machine, with 20 or 30 c.c. of *N*-sodium hydroxide free from carbonate. After fourteen days, a portion of the clear liquid was drawn off without filtration (as filter-paper adsorbs lead in alkaline solution to a considerable extent), and the lead estimated gravimetrically as the sulphate. The solubilities of the various forms (numbered as above) are given in Table I.

TABLE I.

Temperature 20°.

Gram-mol. of PbO *dissolved per litre of N*-NaOH.

	Gentle shaking.	Vigorous shaking.
No. 1.	0·049	0·054
2.	0·048	0·054
3.	0·029	0·033
4.	0·049	
5.	0·049	
6.	0·047	
7.	0·049	
8.	0·040	

Solubility of the Reddish-brown and Yellow Forms.—The identical solubility of the yellow and reddish-brown forms may be explained on the assumption that the yellow agglomerates break down into small particles which are identical with those present in the reddish-brown forms. If these solutions of the reddish-brown and yellow forms were kept in contact with the respective oxides, a slow decrease in solubility was noted from 0·054 to 0·047 gram-mol. per litre, and in some cases to 0·042 gram-mol. per litre. The rate of decrease depended on the previous history of the specimen (that is, on the amount of very finely divided matter present) and on the ratio of solid phase to liquid phase present. In some cases a considerable time elapsed before the decrease became manifest, but in every case where the yellow or reddish-brown oxides were left in contact (without shaking) with *N*-sodium hydroxide containing 0·050 gram-mol. of lead oxide per litre, this decrease was eventually noticed. The equilibrium solubility of these forms is evidently lower than the values obtained with shaking; during the shake, small particles are being continually rubbed off, and high solubility values are therefore obtained, but when the solution is at rest these particles gradually disappear, being redeposited on the larger ones, and the solubility value falls.

In order to determine the equilibrium solubility of the reddish-brown and yellow forms, shaking must be avoided, so an arrangement was made by which the liquid could be gently stirred over the surface of the solid without disturbing the latter. Air free from carbon dioxide and saturated with water vapour to the extent of the vapour pressure of *N*-sodium hydroxide, was gently bubbled through a bottle containing (*a*) yellow lead monoxide and *N*-sodium hydroxide, and (*b*) reddish-brown lead monoxide and *N*-sodium hydroxide. The experiment was carried out at room temperature, which did not vary very much from 20°. Portions of the clear liquor were withdrawn after every three or four days and analysed until constant values were obtained.

In both cases the solubility reached 0·039 gram-mol. of lead oxide per litre, and this may be taken as the solubility of the majority of the particles present in the reddish-brown and yellow forms of lead monoxide.

Solubility of the Red Form.—In this case the solubility showed a tendency to increase with keeping, possibly due to the slow solubility of the red form. More definite values should thus be obtained by placing *N*-sodium hydroxide supersaturated with respect to the red lead oxide in contact with the solid red form; the lead oxide content of the solution should then decrease until the equilibrium value is reached.

N-Sodium hydroxide was saturated with lead oxide to the extent of 0·048 gram-mol. per litre by shaking with the reddish-brown form, and a quantity of the red lead monoxide was placed in this solution. The mixture was gently stirred by the air-current method, and solubility determinations were made from time to time. The final value obtained in this way was 0·035 gram-mol. of lead oxide per litre, which is taken as the solubility of the red lead oxide in *N*-sodium hydroxide. This difference in solubility found between the various forms, namely, 0·039 and 0·035, is one that is readily accounted for on the grounds of varying size of particles. We have already seen that the red form of lead monoxide, if ground, gives a brown powder with a solubility of 0·040 gram-mol. per litre in *N*-sodium hydroxide (Table I).

Jones (*Zeitsch. physikal. Chem.*, 1913, **82**, 448) has developed a formula connecting the solubility of a finely-divided powder with the size of the particles, which resembles that of Ostwald (*ibid.*, 1900, **34**, 495), except that the integer 2 replaces 3. The later formula is simplified for the purpose of the subject now under discussion in the form:

$$\frac{RT}{M}\log_e\frac{s_r}{s_\infty}=\frac{2\sigma}{r\rho}$$

where R, T have their usual meaning, M is the molecular weight of the dissolved substance, σ the energy per unit surface of separation of solid and solution, ρ the density of the solid, s_r and s_∞ the concentrations of the solute when spherical particles of radius r, and plane surfaces of the solid are in contact with the solution; s_∞ is the solubility in a normally saturated solution (Hulett and Allen, *loc. cit.*). In the present case, if we assume that in the red form the particles are large enough to be considered to have plane surfaces, we can put s_∞ as equal to 0·035 gram-mol. per litre. Specimens of reddish-brown and yellow lead monoxide contain particles $0{\cdot}7\mu$ in diameter, and we will assume that it is these particles which give the measured solubility of 0·039 gram-mol. per litre. By substituting these values for s_r and s_∞, and putting $r = 0{\cdot}35 \times 10^{-4}$ cm., $R = 8{\cdot}31 \times 10^7$ ergs, M (for lead oxide) $= 223$, $\rho = 9$ (approx.), and $T = 293°$ Abs., we obtain for σ, the energy located at the surface of discontinuity between lead monoxide and N-sodium hydroxide, the value 1860 ergs per sq. cm. at 20°. This value is of the same order as those calculated for other substances by Jones (*loc. cit.*). The value of σ between lead monoxide and water is probably not very different from the value calculated for N-sodium hydroxide, as the ratio of the solubilities is almost the same in both solvents for particles of equal size (see below).

It may be emphasised here that the explanation of solubility differences that has been developed, is put forward not only for the reddish-brown forms of lead monoxide, but also for the yellow and greenish-yellow forms which have been presumed to be polymorphic modifications by previous authors.

Dissociation Constant of Lead Monoxide as an Acid.

Berl and Austerweil (*Zeitsch. Elektrochem.*, 1907, **13**, 165) calculated the dissociation constant of lead monoxide as a monobasic acid, from the values of its solubility in sodium hydroxide solutions of varying concentrations. This result is incorrect for two reasons, (*a*) the solubility values used were those obtained after vigorous shaking for some hours, and (*b*) the solubility of lead monoxide in water as used by these authors is much too high (compare Pleissner, *Arb. Kaiser. Gesundh.-Amt.*, 1907, **26**, 384). A series of determinations of the solubility of lead monoxide in solutions of sodium hydroxide was therefore carried out by the method described on page 1693. Solutions of sodium hydroxide (free from carbon dioxide) of varying concentrations were shaken with dry lead hydroxide in order to obtain solutions supersaturated with respect to the monoxide (the small amount of water added in this way was regarded as negligible). The clear liquids were drawn off into bottles containing the red lead monoxide, which were then placed in a thermostat at 25°. The solutions were analysed from time to time, until constant values were obtained.

In the more concentrated solutions the lead was estimated as sulphate. With sodium hydroxide solutions of normality 0·2 or less, the lead was precipitated as peroxide by means of bromine water, the precipitate was well washed with boiling water (cold water tends to give colloidal filtrates), and the lead estimated iodometrically.

TABLE II.

All concentrations are expressed in gram-mol. per litre at 25°.

Concn. of NaOH. (C)	PbO in solution. (c_1).	Sodium plumbite. (c_1-c_0).	Residual NaOH. ($C-c_1+c_0$).	$k=\frac{\text{Concn. of HPbO}_2'}{\text{Concn. of OH}'}=\frac{(c_1-c_0)}{(C-c_1+c_0)}$.
0·9985	0·0349	0·03464	0·9639	0·0359
0·4993	0·0195	0·01924	0·4801	0·0401
0·1177	0·00506	0·00481	0·1129	0·0425
0·0499	0·00230	0·00204	0·0479	0·0426

The solution of lead oxide in sodium hydroxide may be represented by the equation

$$\text{PbO (solid)} + \text{OH}' \rightleftharpoons \text{HPbO}_2'$$

(Berl and Austerweil, *loc. cit.*; Hantzsch, *Zeitsch. anorg. Chem.*, 1902, **30**, 305), the equilibrium constant being given by

$$k = [\text{HPbO}_2']/[\text{OH}'].$$

The concentration of plumbite ion ($HPbO_2'$) may be assumed equal to the additional solubility of lead monoxide in sodium hydroxide solution, over and above that of the ordinary solubility in water, multiplied by the degree of ionisation of sodium plumbite at each concentration. If c_1 is the solubility of lead monoxide in sodium hydroxide of concentration C, α_1 and α the degrees of dissociation of plumbite and hydroxide solutions respectively, and c_0 the solubility of lead oxide in water, we have

$$[\text{HPbO}_2'] = (c_1 - c_0)\alpha_1.$$

The total concentration of OH′ originally present is given by $C\alpha$, but as a certain quantity is used up in forming plumbite, the actual concentration is given by $(C - c_1 + c_0)\alpha$. Since sodium hydroxide and plumbite contain a common ion, they will probably be ionised to the same extent in a solution containing both of them. For purposes of calculation we will assume that α and α_1 are equal, an assumption which may not be quite true in the more concentrated solutions. We thus obtain the expression, $k = \frac{(c_1 - c_0)}{(C - c_1 + c_0)}$.

In connexion with the solubility in water of lead monoxide, there is some uncertainty. Pleissner has shown that determinations of solubility by the conductivity method are useless, and only those in which lead has been estimated by chemical methods are worth consideration. Berl and Austerweil (*loc. cit.*) found a solubility of $1{\cdot}02 \times 10^{-3}$ gram-mol. per litre for lead oxide made by heating lead carbonate at 400°. This figure is very much higher than any other to be found in the literature for the solubility of lead oxide in water, and is possibly due to exceptional fineness of division. Milbauer (*Chem. Zeit.*, 1909, **33**, 960) has found that the lead oxide prepared from lead carbonate absorbs oxygen in the formation of red lead, far more rapidly than any other form of the monoxide: this fact confirms the above suggestion. The value for the solubility of lead oxide used in these calculations was obtained as follows. In some work to be published later, the author has found that the ratio of the solubilities of lead hydroxide and the red monoxide in sodium hydroxide of the same concentration is about 1·75 and is almost independent of the concentration of the sodium hydroxide. Assuming this ratio to hold in the case of water, and using Pleissner's (*loc. cit.*) most trustworthy value for the solubility of lead hydroxide, $0{\cdot}45 \times 10^{-3}$ gram-mol. per litre (at 18°), we arrive at a value of $0{\cdot}25 \times 10^{-3}$ gram-mol. per litre for the solubility of the red lead monoxide. This value agrees very well with Berl and Austerweil's value for the solubility of lead oxide in water at 18°, $0{\cdot}26 \times 10^{-3}$ gram-mol. per litre. Although these authors did not use this value, it is probably the most accurate available and will be used in these calculations for 25°; the difference of temperature will not cause serious errors. Attention may be directed to the fact that Pleissner obtained for the solubility of the yellow form a value of $0{\cdot}30 \times 10^{-3}$ gram-mol. per litre; the ratio between this and $0{\cdot}26 \times 10^{-3}$ is not very greatly different from that of 39 to 35, the ratio of the solubilities of the red and yellow forms of lead oxide in N-sodium hydroxide.

Using the values as explained, we arrive at the fifth column of Table II for the value of the equilibrium constant k. The first value 0·0359 is probably low for the reason that α and α_1 are not equal in the more concentrated solution. The value for the constant k to be used in these calculations is 0·0425.

Lead monoxide in solution may be considered as follows:

$$PbO + H_2O \rightleftharpoons Pb(OH)_2 \rightleftharpoons H^{\cdot} + HPbO_2{}'$$

(Hantzsch, *loc. cit.*), and the dissociation constant as an acid is given by

$$K_A = \frac{[H^{\cdot}][HPbO_2{}']}{[Pb(OH)_2]} = \frac{K_w[HPbO_2{}']}{[Pb(OH)_2][OH']} = \frac{K_w k}{[Pb(OH)_2]}$$

where K_w, the dissociation constant of water, is $0{\cdot}81 \times 10^{-14}$ at 25°. The value of $[Pb(OH)_2]$ is taken as equal to the solubility of lead monoxide in water; substituting this and the known values of K_w and k, we obtain $K_A = 1{\cdot}32 \times 10^{-12}$.

Summary.

(1) The suggestion is put forward that the yellow forms of lead monoxide are really agglomerates of small particles, which are almost identical with the finely divided red form. Solubility determinations and microscopic examination confirm this view.

(2) The energy at the surface of separation of lead monoxide and N-sodium hydroxide is calculated as 1860 ergs per sq. cm. at 20°. If water replaces sodium hydroxide solution, the value does not differ greatly.

(3) The dissociation constant of the acid $H{\cdot}HPbO_2$, produced by dissolving lead oxide in water, is $1{\cdot}32 \times 10^{-12}$ at 25°.

The author wishes to thank Professor Allmand for suggesting this series of investigations, and for criticism and advice given throughout the course of this work.

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CXCIII.—*The Mechanism of the Action of Fused Alkalis. Part II. The Action of Fused Potassium Hydroxide on Phenylglyceric Acid.*

By (the late) Henry Rondel Le Sueur and Cyril Christian Wood.

The conversion of dihydroxystearic acid (I) into α-hydroxy-α-octylsebacic acid (III) by the action of molten potassium hydroxide (Le Sueur and Withers, T., 1914, **105**, 2800) involves the preliminary formation of a dihydroxyoctyldecoic acid (II) isomeric with the first-named substance, followed by oxidation:

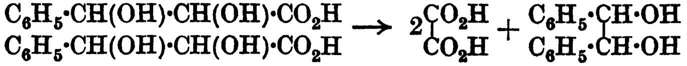
$$C_8H_{17}{\cdot}CH(OH){\cdot}CH(OH){\cdot}C_7H_{14}{\cdot}CO_2H \quad \text{(I.)} \longrightarrow$$
$$HO{\cdot}CH_2{\cdot}C(C_8H_{17})(OH){\cdot}C_7H_{14}{\cdot}CO_2H \quad \text{(II.)} \longrightarrow$$
$$CO_2H{\cdot}C(C_8H_{17})(OH){\cdot}C_7H_{14}{\cdot}CO_2H \quad \text{(III.)}$$

By similar transformations, dihydroxybehenic acid was converted into α-hydroxy-α-octyldodecanedicarboxylic acid (*loc. cit.*), and it was therefore resolved to ascertain whether phenylglyceric acid

(IV), in which the octyl group is replaced by phenyl, and the remaining unsubstituted aliphatic chain is eliminated, would undergo conversion into phenyltartronic acid (V), or products of its decomposition :

$$C_6H_5\cdot CH(OH)\cdot CH(OH)\cdot CO_2H \text{ (IV.)} \longrightarrow$$
$$HO\cdot CH_2\cdot C(C_6H_5)(OH)\cdot CO_2H \longrightarrow CO_2H\cdot C(C_6H_5)(OH)\cdot CO_2H \text{ (V.)}$$

It soon became evident that the change takes an entirely different course, neither phenyltartronic acid, nor degradation products therefrom such as phenylglycollic acid and benzyl alcohol, being obtained. At a temperature approaching 250° approximately equivalent amounts of benzoic and oxalic acids were produced, whilst under less drastic treatment (160—170°) the principal aromatic product was toluene, accompanied by an equivalent amount of oxalic acid and very much smaller quantities of benzoic, formic, and acetic acids; in each case 30—40 per cent. of the original material was lost. On heating the system at the lower temperature under reduced pressure, however, a remarkable alteration in the course of the change was effected, the aromatic group appearing as *iso*hydrobenzoin (VI), accompanied by nearly two molecular proportions of oxalic acid and a subsidiary quantity of benzoic acid :



$$\begin{array}{l} C_6H_5\cdot CH(OH)\cdot CH(OH)\cdot CO_2H \\ C_6H_5\cdot CH(OH)\cdot CH(OH)\cdot CO_2H \end{array} \longrightarrow 2\begin{array}{l} CO_2H \\ | \\ CO_2H \end{array} + \begin{array}{l} C_6H_5\cdot CH\cdot OH \\ \qquad\ \ | \\ C_6H_5\cdot CH\cdot OH \end{array} \text{ (VI.)}$$

Under the conditions observed, almost all the water was removed from the system before the temperature had reached 150°, and as the visible action does not begin below that stage, it seems highly probable that the great divergence from previous experiments must be due to this cause. Examination was made for tartaric acid, which might have been expected to accompany *iso*hydrobenzoin, but that substance could not be found.

The formation of toluene would be explained by simultaneous reduction and oxidation, recalling that by which benzyl alcohol and benzoic acid arise together from benzaldehyde, leading in this case to phenylpyruvic acid (VII) as an intermediate stage :

$$C_6H_5\cdot CH(OH)\cdot CH(OH)\cdot CO_2H \longrightarrow C_6H_5\cdot CH_2\cdot CO\cdot CO_2H \longrightarrow$$
$$C_6H_5\cdot CH_3 + (CO_2H)_2.$$

Search was accordingly made for phenylpyruvic acid, but it was only when phenylglyceric acid was heated under reflux during many hours with a concentrated solution of potassium hydroxide that a small quantity of material giving the characteristic coloration with ferric chloride was obtained.

The profound alterations consequent on varying the conditions of the foregoing oxidation emphasise once more the uncertainty of molten potassium hydroxide in its action on organic substances, the result of which can be accepted only as corroborative evidence in questions of constitution when harmonising with those from sources less under suspicion.

EXPERIMENTAL.

A preliminary experiment showed that the action of fused potassium hydroxide on phenylglyceric acid does not give rise to effervescence until a temperature approaching 150° is reached, when the odour of toluene is noticeable; thereafter, at about 180°, the action becomes difficult to control, and the pasty mass remaining after nine minutes have elapsed in reaching 200° contains potassium benzoate and oxalate. More precise conditions were therefore defined.

At a Temperature of 160—170^{c}.—Ten grams of phenylglyceric acid with 50 grams of potassium hydroxide and 20 c.c. of water in a retort connected with a condenser were heated during fifty-four minutes by a bath of fusible metal at 160—170°, action at first being very vigorous. Toluene (3·3 grams) passed over in the steam and, when isolated, distilled completely at 110—111° (Found: $C = 91·3$; $H = 8·8$. C_7H_8 requires $C = 91·3$; $H = 8·7$ per cent.). The residue in the retort having been dissolved in water, aliquot parts of the solution were examined separately and quantitatively for benzoic, and for oxalic and formic acids, the amounts estimated being 0·68, 3·4, and 0·11 gram respectively; the presence of acetic acid was demonstrated qualitatively. Hence the toluene and oxalic acid were produced in equivalent amounts, and the extent of conversion was about 68 per cent.

At a Temperature of 240—250°.—Potassium hydroxide (50 grams) and water (20 c.c.) in a nickel crucible were heated by fusible metal, and when the temperature had reached 240—250° phenylglyceric acid (10 grams) was added in small quantities with continued stirring during twenty minutes, liberation of benzoic acid vapour being recognisable. The cold, faintly green product was dissolved in 150 c.c. of water and acidified with 68 c.c. of hydrochloric acid, when benzoic acid was precipitated; the quantity, making allowance for solubility in water, amounted to 4 grams, and the filtrate contained 3·1 grams of oxalic acid. Thus the acids were produced in approximately equivalent amounts, the deficit of benzoic acid being doubtless due to volatilisation during fusion; the extent of conversion was about 60 per cent.

At 170—180°, *under Reduced Pressure.*—Phenylglyceric acid (5 grams), potassium hydroxide (25 grams), and water (10 c.c.) were heated in a distilling flask which was evacuated through a condenser. By controlling the temperature of the castor-oil bath at 170—180°, the pressure was maintained during ten minutes at 25 mm., but this reduction was not reached until almost all the water had been removed. The oil which distilled was negligible, and the colourless residue in the flask having been extracted with water and acidified, *iso*hydrobenzoin (1·9 grams), benzoic acid (0·2 gram), and oxalic acid (1·2 grams) were recognised. Thus the quantity of *iso*hydrobenzoin indicated a conversion of 65 per cent., but the amount of oxalic acid, whilst exceeding one equivalent, fell somewhat short of that corresponding with two molecular proportions.

Since benzoic acid and *iso*hydrobenzoin melt at the same temperature (121°), identity of the latter substance was established by analysis and by determination of molecular weight in boiling acetone (Found: $C = 78·60$; $H = 6·59$. $M = 213$. $C_{14}H_{14}O_2$ requires $C = 78·50$; $H = 6·54$ per cent. $M = 214$). The diacetyl derivative melted at 117—118° (Found: $C = 72·29$; $H = 6·07$. $C_{18}H_{18}O_2$ requires $C = 72·48$; $H = 6·04$ per cent.).

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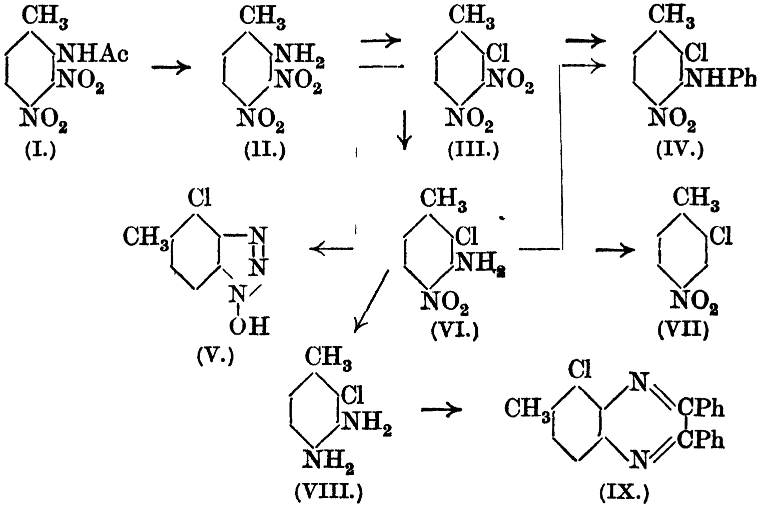
CXCIV.—ortho-*Chlorodinitrotoluenes. Part IV.*
2-Chloro-3 : 4-dinitrotoluene.

By GILBERT T. MORGAN and THOMAS GLOVER.

IN an earlier communication (T., 1920, **117**, 784) the number of known *o*-chlorodinitrotoluenes was increased from two to four, these isomerides being obtained by nitrating *o*-chlorotoluene or its mononitro-derivatives. The remaining two isomerides may also occur to a small extent among the crude nitration products, but hitherto these compounds have escaped detection.

2-Chloro-3 : 4-dinitrotoluene (III), melting at 89°, has now been prepared indirectly by the Sandmeyer reaction from 3 : 4-dinitro-*o*-toluidine (II), a base recently described by Brady and Williams (T., 1920, **117**, 1137), and with the isolation of this new isomeride the three theoretically possible *o*-dinitro-derivatives of *o*-chlorotoluene have been obtained, so that the reactions of this set of closely related isomerides may be compared.

When treated with ammonia or aniline, 2-chloro-3 : 4-dinitrotoluene readily furnishes an amine in which the 3-nitro-group is replaced quantitatively by the basic radicle. 2-*Chloro*-4-*nitro*-m-*toluidine* (VI) and 2-*chloro*-4-*nitro*-N-*phenyl*-m-*toluidine* (IV) are obtained respectively, and the orientation of the amino- and phenylamino-groups has been demonstrated by the methods summarised in the following diagram :

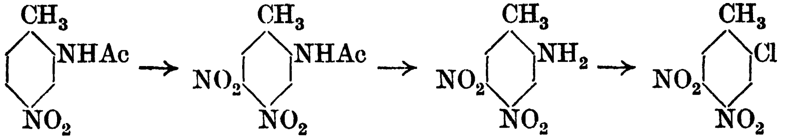


It is noteworthy that the two consecutively substituted isomerides, 2-chloro-3 : 4-dinitrotoluene and 2-chloro-5 : 6-dinitrotoluene, having the two contiguous nitro-groups at one end or the other of the consecutive series of substituents each lose the interior (3- or 6-) nitro-group only and give rise to one amine (IV and VI) when treated with ammonia or aniline. On the contrary, 2-chloro-4 : 5-dinitrotoluene, which has its contiguous nitro-groups separated from the other substituents, furnishes on treatment with ammonia a mixture of amines, as recently demonstrated (this vol., p. 1537), showing that each nitro-group in this isomeride is possessed of a certain degree of lability.

Hydrazine hydrate reacts with 2-chloro-3 : 4-dinitrotoluene giving 4-*chloro*-1-*hydroxy*-5-*methyl*-1 : 2 : 3-*benzotriazole* (V), in which it is assumed, from analogy with the condensation with ammonia, that this diamine replaces the 3-nitro-group and condenses with the 4-nitro-group to complete the triazole ring. 2-*Chloro*-3 : 4-*tolylenediamine* (VIII), obtained by the reduction of 2-chloro-4-nitro-*m*-toluidine, gives the typical reactions of an ortho-diamine, condensing with benzil to yield 5-chloro-2 : 3-diphenyl-6-methylquinoxaline (IX).

These condensations show that the two nitro-groups in 3 : 4-

dinitro-*o*-toluidine are actually in *ortho*-positions to one another, and since the starting point in these researches is 4-*nitroaceto*-o-*toluidide* (X), it follows that the entrant nitro-group must be in position 3 or 5. The latter position is excluded because of the simultaneous formation of the isomeric 3 : 4- and 4 : 5-dinitroaceto-*o*-toluidides (I and XI) (Brady and Williams, *loc. cit.*). The latter acetyl-4 : 5-dinitro-derivative, on hydrolysis, gives 4 : 5-dinitro-*o*-toluidine (XII), which has now (p. 1703) been converted into 2-chloro-4 : 5-dinitrotoluene (XIII). Since the other dinitro-*o*-toluidine (II) derived from 4-nitroaceto-*o*-toluidide (X) leads to an *ortho*-diamine (VIII), it follows that the entrant nitro-group is in position 3. The constitution of the new 2-chloro-3 : 4-dinitrotoluene is therefore completely demonstrated.



(X.) (XI.) (XII.) (XIII.)

EXPERIMENTAL.

The nitration of 4-nitroaceto-*o*-toluidide was carried out by the method described by Brady and Williams (*loc. cit.*), and the mixture of 3 : 4-dinitro- and 4 : 5-dinitro-aceto-*o*-toluidides was hydrolysed and separated as follows. Ninety-two grams of the mixture were heated for six hours on the water-bath with 360 c.c. of concentrated sulphuric acid diluted with 720 c.c. of water. The precipitate (42 grams) which had separated on cooling was washed successively with 50 per cent. sulphuric acid and with water; it was then crystallised twice from absolute alcohol and twice from 50 per cent. alcohol, when purified 3 : 4-dinitro-*o*-toluidine (32 grams) was obtained, melting at 130°.

The acid filtrate from the crude 3 : 4-dinitro-compound, when diluted with water, furnished 17 grams of crude 4 : 5-dinitro-*o*-toluidine, which, after repeated crystallisation from alcohol, melted at 190°, the yield of purified base being 13 grams. 3 : 4-*Dinitroaceto*-o-*toluidide* was prepared by adding a drop of concentrated sulphuric acid to 1 gram of 3 : 4-dinitro-*o*-toluidine in 3 c.c. of acetic anhydride; the base dissolved with considerable generation of heat and the greater part of the acetyl derivative crystallised out immediately. Water was then added and the product crystallised repeatedly from dilute acetic acid, when it separated in brittle, yellowish-white needles melting at 186° (Found: N = 17·73.

$C_9H_9O_5N_3$ requires N = 17·57 per cent.). 4 : 5-*Dinitroaceto*-o-*toluidide*, prepared and purified as in the preceding preparation, was obtained in colourless needles melting at 180° (Found : N = 17·80 per cent.).

2-*Chloro*-3 : 4-*dinitrotoluene* (III).

Twenty grams of 3 : 4-dinitro-*o*-toluidine, 50 c.c. of concentrated hydrochloric acid, and 300 c.c. of absolute alcohol were heated on the water-bath for thirty minutes and treated with 100 c.c. of 10 per cent. cuprous chloride, prepared by reducing with copper 10 grams of copper carbonate in 100 c.c. of concentrated hydrochloric acid. To the warm solution at 70°, 30 grams of sodium nitrite in 100 c.c. of water were slowly added from a tap-funnel dipping below the surface of the liquid. The alcohol was evaporated and the residual oil allowed to solidify over-night to a brown mass, which was washed with water, dissolved in absolute alcohol, and the solution taken to dryness on the water-bath. The dried residue was extracted three times with 60 c.c. of boiling petroleum (b. p. 80°). This extract was concentrated to 20 c.c., when an oil separated which solidified on cooling. The product, after draining on porous tile, was dissolved in 50 c.c. of boiling glacial acetic acid, the solution cooled to 60°, and diluted with water until cloudy. The solid which separated on cooling was repeatedly submitted to this process with acetic acid and water until pure 2-chloro-3 : 4-dinitrotoluene was obtained. The filtrates at each stage of the process were diluted further with water to obtain additional crops of the product.

2-*Chloro*-3 : 4-*dinitrotoluene*, obtained by this process of purification, separated in colourless needles melting at 89°; a mixed melting point with an equal weight of 2-chloro-4 : 5-dinitrotoluene (m. p. 88·5°) gave 55° (Found: N = 13·28, 13·14; Cl = 16·58. $C_7H_5O_4N_2Cl$ requires N = 12·93; Cl = 16·37 per cent.).

2-Chloro-3 : 4-dinitrotoluene dissolved readily in acetone, benzene, chloroform, or acetic acid, but was more sparingly soluble in petroleum. The following colour changes were observed: with warm aqueous sodium hydroxide, yellow (transparent), yellowish-brown (tr.), brownish-red (tr.); with alcoholic sodium hydroxide, pale green (tr.), dark green (tr.), greenish-black (opaque), brownish-black (op.) and after heating and leaving for two hours, pale red (tr.); with alcoholic ammonia, faint yellow (tr.).

2-*Chloro*-4 : 5-*dinitrotoluene from* 4 : 5-*Dinitro*-o-*toluidine*.

The foregoing experiment was repeated on 4 : 5-dinitro-*o*-toluidine; the crude chloro-compound was extracted successively with alcohol, petroleum (b. p. 80°), and dilute acetic acid. Repeated crystallisation from the last of these solvents yielded 2-chloro-4 : 5-dinitrotoluene in colourless needles melting at 87°. This product was identified by a mixed melting point with a specimen obtained by nitrating 2-chloro-4-nitrotoluene.

Reactions of 2-Chloro-3 : 4-dinitrotoluene with Bases.

(1) *2-Chloro-4-nitro-*m*-toluidine* (VI).—2-Chloro-3 : 4-dinitrotoluene was dissolved and left for fourteen days in about sixty parts of absolute alcohol saturated with ammonia. The solution acquired a yellow colour, and on dilution with an equal bulk of water gave a yellow solid which, after two crystallisations from dilute alcohol, separated in lustrous, golden-yellow needles melting at 105°; the yield was quantitative (Found : $N = 14{\cdot}94$. $C_7H_7O_2N_2Cl$ requires $N = 15{\cdot}02$ per cent.).

2-Chloro-4-nitro-*m*-toluidine was readily soluble in alcohol, acetone, chloroform, or benzene, but dissolved less readily in light petroleum. With alcoholic sodium hydroxide, it gave a deep orange-red coloration.

The substitution of the amino-group for the 3-nitro-radicle in 2-chloro-3 : 4-dinitrotoluene was demonstrated in the following manner: 2-Chloro-4-nitro-*m*-toluidine (0·4 gram) was dissolved in a mixture of 7 c.c. of concentrated sulphuric acid and 3 c.c. of water; 0·4 gram of powdered sodium nitrite was added slowly to the mixture cooled to −5°. Small fragments of ice were then gradually introduced, the nitrite dissolved, and when 20 grams of ice were added the diazotisation was complete. The solution was then added to 20 c.c. of boiling alcohol and the mixture boiled for a few minutes. The alcohol was evaporated and the residue distilled in steam. The oily distillate solidified, and was identified as 2-chloro-4-nitrotoluene by a mixed melting point with a standard specimen (m. p. 65°). The alcoholic distillate and the residue in the distilling-flask gave further quantities of 2-chloro-4-nitrotoluene, the total yield being 70 per cent.

(2) *2-Chloro-4-nitro-*N*-phenyl-*m*-toluidine* (IV).—2-Chloro-3 : 4-dinitrotoluene (0·75 gram) and 2 c.c. of aniline were dissolved in 50 c.c. of absolute alcohol and boiled under reflux for twenty hours. The solution became successively yellow and dark red, while a tarry product separated. Water and dilute hydrochloric acid were then added, the excess of aniline was dissolved, and the solid residue, which acquired a pink colour, crystallised in succession from alcohol and petroleum (b. p. 80°); the latter solvent did not dissolve the tar. The orange-red residue from the petroleum extract was

crystallised repeatedly from dilute alcohol, when it separated in orange-red needles melting at 95° (Found: N = 10·78. $C_{13}H_{11}O_2N_2Cl$ requires N = 10·67 per cent.).

2-Chloro-4-nitro-*N*-phenyl-*m*-toluidine was readily soluble in acetone, chloroform, benzene, or alcohol, but less soluble in light petroleum. In hot concentrated sulphuric acid, this base developed successively violet, purplish-red, deep red, and, finally, brownish-black colorations. The orientation of the phenylamino-group in the preceding base was demonstrated as follows:

2-Chloro-4-nitro-*m*-toluidine (0·2 gram), 1 c.c. of bromobenzene, 0·1 gram of anhydrous potassium carbonate, and a trace of cuprous iodide in 10 c.c. of nitrobenzene were boiled under reflux for twenty hours. The dark reddish-brown solution was distilled in steam to remove nitrobenzene and excess of bromobenzene, and the residual oil dissolved in absolute alcohol. The alcoholic extract was evaporated to dryness and the residue extracted repeatedly with hot petroleum (b. p. 80°). This extract was also evaporated to dryness and the residue crystallised repeatedly from dilute alcohol, when orange-yellow needles were obtained melting at 89°. This melting point was not depressed by mixing the product with the pure 2-chloro-4-nitro-*N*-phenyl-*m*-toluidine (m. p. 95°). Hence the two preparations give rise to identical substances and the orientation of the *N*-phenylamino-group in position 3 is confirmed.

2-Chloro-3 : 4-dinitrotoluene did not condense with *m*-nitroaniline to give a substituted tolylphenylamine derivative, in this respect differing from 2 : 3 : 4-trinitrotoluene, which condenses with *m*-nitroaniline on prolonged heating (*Proc. Roy. Irish Acad.*, 1918, **31**, 103).

(3) 4-*Chloro*-1-*hydroxy*-5-*methyl*-1 : 2 : 3-*benzotriazole* (V).—Hydrazine hydrate (0·5 c.c. of 50 per cent. solution) dissolved in 1·5 c.c. of absolute alcohol was added to 0·5 gram of 2-chloro-3 : 4-dinitrotoluene in 4 c.c. of boiling alcohol. The solution reddened, a vigorous reaction set in lasting about a minute, and the liquid became yellow. On cooling, the mixture became semi-solid from the separation of a colourless, crystalline product, which, after recrystallisation from absolute alcohol, separated in colourless needles decomposing somewhat indefinitely at 218—225° (Found: N = 32·61. The *hydrazine* salt, $C_7H_6ON_3Cl,N_2H_4$, of the hydroxytriazole requires N = 32·49 per cent.).

The concentrated aqueous solution of this hydrazine salt was acidified with hydrochloric acid, when the hydroxytriazole separated. It crystallised from dilute alcohol in colourless, hexagonal plates darkening at 208° and melting with vigorous decomposition at

210—212° (Found: N = 22·95. $C_7H_6ON_3Cl$ requires N = 22·88 per cent.).

This hydroxytriazole was sparingly soluble in cold water, but dissolved readily in alcohol; its hydrazine salt was very soluble in cold water, and sparingly soluble in cold alcohol; it deflagrated on heating.

2-*Chloro*-3 : 4-*tolylenediamine* (VIII).

Zinc dust (0·5 gram) and 0·4 gram of ammonium chloride were added to 0·8 gram of 2-chloro-4-nitro-*m*-toluidine in 12 c.c. of alcohol and 4 c.c. of water. The mixture was refluxed for thirty minutes, another 0·5 gram of zinc dust was added, and the heating continued for a further thirty minutes, when the greenish-brown liquid had become colourless. The zinc dust was quickly filtered and the filtrate cooled in a freezing mixture and saturated with hydrogen chloride. The precipitated hydrochloride was dissolved in cold, strong, aqueous sodium hydroxide, when the free diamine separated as a light brown oil which quickly solidified. Repeated crystallisation from petroleum (b. p. 80°) yielded the diamine in pale brown needles melting at 55—56° (Found: N = 17·92. $C_7H_9N_2Cl$ requires N = 17·89 per cent.).

2-*Chloro*-3 : 4-*tolylenediamine* was very soluble in the ordinary organic media excepting light petroleum; it was readily oxidised when its alcoholic solution was exposed to air.

5-*Chloro*-2 : 3-*diphenyl*-6-*methylquinoxaline* (IX).

One gram of 2-chloro-4-nitro-*m*-toluidine was reduced to 2-chloro-3 : 4-tolylenediamine and the crude diamine added to 1 gram of benzil in 10 c.c. of warm alcohol, the mixture being refluxed for one and a half hours. On cooling the yellow solution, the quinoxaline separated as a pale yellow solid which, after two crystallisations from alcohol, was obtained in clusters of yellowish-white needles melting at 143° (Found: N = 8·69. $C_{21}H_{15}N_2Cl$ requires N = 8·47 per cent.). This quinoxaline developed a red coloration with cold concentrated sulphuric acid.

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CXCV.—*Dinaphtha*-1 : 7 : 1′ : 7′-*diquinone.*

By GILBERT T. MORGAN and DUDLEY CLOETE VINING.

ALTHOUGH at least six naphthaquinones are theoretically possible, only three have so far been isolated, namely, α- or 1 : 4-naphthaquinone, β- or 1 : 2-naphthaquinone, and *amphi*- or 2 : 6-naphthaquinone, all of which can be obtained by the oxidation of the corresponding dihydroxynaphthalenes. The *peri*- or 1 : 8-naphthaquinone of Meldola and Hughes was subsequently shown by Liebermann and Schlossberg to be 2 : 2′-dinaphtha-1 : 4 : 1′ : 4′-diquinone (T., 1890, **57**, 393, 631; *Ber.*, 1899, **32**, 546, 868), and there is at present little evidence for the existence of derivatives of the 1 : 8-quinone (compare Quincke, *Ber.*, 1888, **21**, 1460). Derivatives of 2 : 3-naphthaquinone have been described, for example, 4-chloro-6-bromo-1-methyl-2 : 3-naphthaquinone (Fries and Empson, *Ber.*, 1909, **42**, 3375).

In addition to the three naphthaquinones there are known to be two diquinones containing dinaphthyl residues, namely, 1 : 1′-dinaphtha-3 : 4 : 3′ : 4′-diquinone (Stenhouse and Groves, *Annalen*, 1878, **194**, 205; T., 1878, **33**, 415; Zincke and Rathgen, *Ber.*, 1886, **19**, 2483) and 2 : 2′-dinaphtha-1 : 4 : 1′ : 4′-diquinone (Staub and Smith, T., 1885, **47**, 104; Chattaway, *ibid.*, 1895, **67**, 657; Witt and Dedichen, *Ber.*, 1897, **30**, 2663; Liebermann and Schlossberg, *loc. cit.*; Meldola and Hughes, *loc. cit.*). These diquinones are produced by oxidising various compounds containing only one naphthalene nucleus and indicate a tendency for two naphthyl residues to coalesce during oxidation.

In 1907, Willstätter and Parnas succeeded in obtaining 2 : 6-naphthaquinone by the oxidation of 2 : 6-dihydroxynaphthalene in hot anhydrous benzene with excess of lead peroxide (*Ber.*, 1907, **40**, 1406), but their paper contains no indication as to whether or not they extended their investigation to other dihydroxynaphthalenes which might be expected to furnish the remaining, theoretically possible naphthaquinones.*

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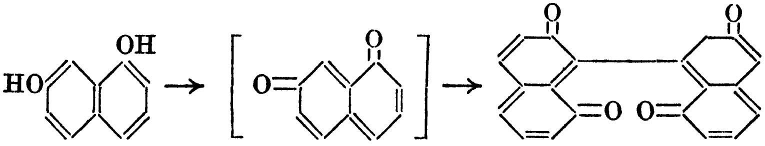
* Since this paper was communicated to the Society, Professor Barger has kindly lent me (G.T.M.) a copy of the dissertation by Parnas (Munich, 1908), from which it appears that oxidation experiments were made on 1 : 7-, 1 : 8-, and 1 : 5-dihydroxynaphthalenes. In the case of the first of these the thesis states :

"Bleisuperoxyd wirkt nicht ein; es wurde bei Oxydationsversuchen damit immer nur wenig unreines Ausgangmaterial zurückgewonnen; nichts liefs auf die Bildung eines Chinons schliefsen."

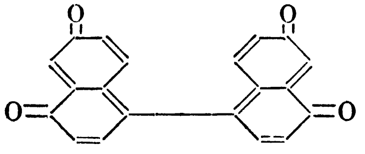
There is also a reference to a transient violet coloration produced by silver oxide on the 1 : 7-isomeride in ethereal solution.

The experiments recorded in the present research were carried out on 1 : 7-dihydroxynaphthalene (I), which on oxidation should yield by a rearrangement of single and double linkings the unknown 1 : 7-naphthaquinone (II)

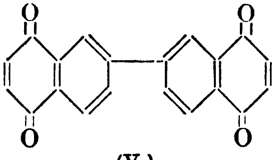


(I.) (II.) (III.)

In this case, however, oxidation proceeded a stage further, and the product obtained in a yield of about 5 per cent. proved to be a new diquinone, *dinaphtha*-1 : 7 : 1′ : 7′-*diquinone,* where the numbering refers to the original orientation of the quinonoid oxygen atoms. It has not been found possible to determine with certainty the positions at which the condensation of the two naphthalene nuclei has occurred, although the steric hindrance noticeable in the formation of *dinaphtha*-1 : 7 : 1′ : 7′-*diquinone-dioxime,* $C_{20}H_{10}O_2(NOH)_2$, suggests a grouping together of the ketonic radicles as shown in formula III. Structural formula IV is not, however, altogether excluded, but the configuration V is rendered very improbable by the fact that the diquinone was not



(IV.)



(V.)

obtained by the oxidation of 1 : 6-dihydroxynaphthalene. If the diquinone is derived from a condensation of 6- or 7-hydroxy-1 : 4-naphthaquinone, then both 1 : 6- and 1 : 7-dihydroxynaphthalenes should yield it.

Dinaphtha-1 : 7 : 1′ : 7′-diquinone forms a well-defined, yellow benzene additive compound, $C_{20}H_{10}O_4,C_6H_6$; the combined hydrocarbon is eliminated on exposure to the atmosphere or more rapidly on warming. The benzene-free diquinone is obtained in pale orange crystals which are thermotropic, becoming bright red on heating to 160°. This colour change is reversed on cooling.

Owing to the small yield of dinaphtha-1 : 7 : 1′ : 7′-diquinone obtainable from 1 : 7-dihydroxynaphthalene the total amount of this oxidation product at our disposal for the following experiments did not exceed 3·5 grams, and on this account the constitution of the diquinone was not completely demonstrated. But preliminary investigations showed that two promising lines of research are suggested by a study of the reduction products of the diquinone.

1 : 7 : 1′ : 7′-*Tetrahydroxydinaphthyl*, $C_{20}H_{10}(OH)_4$, is produced almost quantitatively by reducing the diquinone with amalgamated aluminium or hydriodic acid. The diquinone is not reduced by sulphurous acid, but distillation with zinc dust leads to the formation of an extremely stable, volatile substance subliming and crystallising in yellow needles; this product is probably a quinonoid compound arising from the partial deoxidation of the diquinone.

EXPERIMENTAL.

1 : 7-*Dihydroxynaphthalene* (Emmert, *Annalen*, 1887, **241**, 371).—The crocein salt (sodium β-naphthol-8-sulphonate) employed as the starting material in these experiments was presented to us by the British Dyestuffs Corporation, to whom and to Mr. J. Baddiley of this firm our best thanks are tendered. Four hundred grams of 64 per cent. crocein salt were added during thirty minutes to 1,200 grams of fused potassium hydroxide at 230—240°. The temperature was then raised to 250° and maintained at 245—255° for thirty minutes, the fused mass being thoroughly stirred. The cooled fusion, broken into small pieces, was dissolved in 2,800 c.c. of water and acidified with 1,840 c.c. of concentrated hydrochloric acid. The tar was separated and extracted in a Soxhlet apparatus with chloroform. The aqueous solution on cooling yielded 1 : 7-dihydroxynaphthalene, and more of this product was obtained by extraction with chloroform. The yield of 1 : 7-dihydroxynaphthalene from tar and aqueous liquors was upwards of 40 per cent. of the theoretical amount. When purified by repeated crystallisation from benzene, 1 : 7-dihydroxynaphthalene was obtained in almost colourless needles melting at 178°.

Lead Dioxide.—A rapid stream of chlorine was passed into a well stirred, aqueous solution (900 c.c.) of lead acetate (190 grams) and sodium hydroxide (100 grams). The chocolate-brown lead dioxide was collected, washed, dried, finely powdered and again dried to constant weight at 120°. This preparation was very active, and ignition accompanied by slight explosions occurred on rubbing the dioxide in contact with organic materials.

Purified Benzene.—Good commercial benzene was treated successively with sulphuric acid, chromic acid mixture, sodium hydroxide, and water. It was then dried over calcium chloride, refluxed over sodium for two hours, and finally distilled fractionally from this metal. These precautions were proved to be necessary, for when 1 : 7-dihydroxynaphthalene was oxidised in benzene containing toluene an appreciable amount of benzoic acid was isolated. This impurity did not appear in benzene freed from toluene.

Oxidation of Dihydroxynaphthalenes with Metallic Peroxides.

The experiments of Willstätter and Parnas were repeated, 200 grams of lead dioxide being used to oxidise 3 grams of 2 : 6-dihydroxynaphthalene, when yields of *amphi*(2 : 6-)naphthaquinone were obtained varying from 10 to 20 per cent. of the calculated amount. On replacing lead dioxide by nickelic oxide, the yield was diminished, and a negative result was obtained on employing the following oxidising mixture (CuO, 1 part; MnO_2, 6 parts; Co_2O_3, 3 parts; Ag_2O, 1 part).

1 : 6-Dihydroxynaphthalene was treated in cold dry benzene with lead dioxide, as described below for the 1 : 7-isomeride. The benzene filtrate was colourless and gave no residue on evaporation; there was no indication of quinone formation, and no unchanged dihydroxynaphthalene could be recovered. The oxidation had evidently taken a different course from that manifested in the following experiment.

Oxidation of 1 : 7-*Dihydroxynaphthalene.*—Preliminary experiments showed that oxidation with lead dioxide in boiling benzene (Willstätter and Parnas, *loc. cit.*) was too violent, the yield of diquinone being only 0·5 to 1 per cent. A more favourable result was obtained as follows: Five grams of finely powdered 1 : 7-dihydroxynaphthalene were added all at once to 125 grams of freshly-prepared, well-dried lead dioxide suspended in pure dry benzene (400 c.c.) at the ordinary temperature; the mixture was shaken continuously for five minutes, when the temperature rose about 5°. The lead dioxide was collected rapidly, drained and returned to the reaction vessel with 100 c.c. of fresh benzene; the mixture was shaken for a further five minutes and filtered rapidly. The united filtrates, which were intensely yellow, were distilled under 20—30 mm. pressure to about 50 c.c., when the diquinone–benzene compound separated in well-defined, transparent, lemon-yellow, flat, elongated four-sided prisms with oblique ends. A further crop was obtained on the addition of petroleum (b. p. 40—60°); the highest yield obtained was 5·3 per cent.

An air-dried specimen of the additive compound, when heated at 100° in a vacuum to constant weight, lost 20·26 per cent. $C_{20}H_{10}O_4,C_6H_6$ requires $C_6H_6 = 19{\cdot}90$ per cent. The orange, benzene-free diquinone gave $C = 76{\cdot}44$; $H = 3{\cdot}71$. $C_{20}H_{10}O_4$ requires $C = 76{\cdot}42$; $H = 3{\cdot}21$ per cent.

Molecular Weight Determinations.—Ebullioscopic method in benzene: w/W = 1·10/100, Δt = 0·085°, whence M = 340; in acetone, w/W = 2·97/100, Δt = 0·176°, whence M = 289.

Microscopic method (Barger, T., 1904, **85**, 286), using acetone as solvent and benzil as standard substance. Comparable determinations were made with two of the simple naphthaquinones.

α-(1 : 4)-Naphthaquinone, M = 159.
β-(1 : 2)-Naphthaquinone, M = 171.
$C_{10}H_6O_2$ requires M = 158.

Dinaphtha-1 : 7 : 1′ : 7′-diquinone,
M = 279.
$C_{20}H_{10}O_4$ requires M = 314.

Dinaphtha-1 : 7 : 1′ : 7′-*diquinone* crystallised from solvents other than benzene in pale orange, square tablets; on heating, it commenced to darken at 110°, and was bright red at 160°. At 214°, it became brown, and melted with decomposition at 217°. On cooling from 160°, the diquinone reverted to the pale orange form. When moistened with benzene or when exposed to the vapour of this hydrocarbon, it became yellow, owing to the formation of the benzene additive compound. The resulting lemon-yellow crystals on exposure to air lost their transparency, and darkened in colour owing to partial loss of benzene; this elimination was completed after six days in a vacuum over paraffin wax. At 100° in a vacuum, the benzene was removed in fifteen minutes.

The diquinone, which was inodorous and non-volatile, dissolved only sparingly in ether, alcohol, acetic acid, ethyl acetate, carbon tetrachloride, carbon disulphide, or chlorobenzene, but was slightly more soluble in benzene (1 in 250 at 20°, 1 in 100 at 80°) or chloroform, and appreciably more so in acetone. With an alcoholic solution of guaiacum resin it developed a blue coloration; with concentrated sulphuric acid a brown, insoluble substance separated. In nitric acid, it became bright red, dissolving to an orange solution, from which a reddish-brown precipitate was deposited on dilution.

In view of the small yield of diquinone, search was made for other products of the oxidation of 1 : 7-dihydroxynaphthalene. The benzene extract contained no other substance; the lead oxide residues gave no organic material on extraction with the ordinary solvents, but on treatment with organic or mineral acids a considerable amount of carbon dioxide was evolved, indicating complete oxidation of dihydroxynaphthalene to a carbonate. The acid liquor was yellow, and on extraction with ether or chloroform yielded a small amount of gummy residue smelling of benzoquinone and of a higher fatty acid. These results also pointed to far-reaching oxidation.

Dinaphtha-1 : 7 : 1′ : 7′-*diquinonedioxime*, $C_{20}H_{10}O_2(NOH)_2$.

Hydroxylamine sulphate (0·35 gram) and potassium hydroxide (0·5 c.c. of 50 per cent. solution) were added in the cold to the benzene-free diquinone (0·25 gram) in 12 c.c. of alcohol. The solution, which reddened immediately, was heated on the water-bath for three hours, cooled, filtered, and concentrated at the ordinary temperature in a vacuum. The dark red, scaly residue, when dissolved in alcohol, yielded on addition of water a red, crystalline powder, which crystallised from aqueous alcohol in brownish-red flakes having no melting point below 300° (Found: N = 8·00. $C_{20}H_{12}O_4N_2$ requires N = 8·13 per cent.). Although more than sufficient hydroxylamine was used to give a tetraoxime, only the dioxime was actually obtained (yield 50 per cent.).

Dinaphtha-1 : 7 : 1′ : 7′-*diquinonetetra*-2 : 4-*dinitrophenylhydrazone*, $C_{20}H_{10}[N{\cdot}NH{\cdot}C_6H_3(NO_2)_2]_4$.

The diquinone (0·2 gram) dissolved in 12 c.c. of hot glacial acetic acid containing 0·52 gram of 2 : 4-dinitrophenylhydrazine to a dark red solution, which after one hour was diluted with water, when a dark purple-brown powder was precipitated. The yellow mother-liquor was concentrated in a vacuum desiccator over soda-lime until a yellow, crystalline powder separated. Recrystallised from aqueous alcohol, this tetrahydrazone appeared in golden-yellow needles melting and decomposing at 193—194°, the yield being about 20 per cent. (Found: N = 22·05. $C_{44}H_{26}O_{16}N_{16}$ requires N = 21·67 per cent.).

The less soluble, purple product (yield about 20 per cent.) was probably a dihydrazone; it separated from aqueous alcohol as a purple-brown, lustrous powder decomposing at 205—206°, but it could not be obtained definitely crystalline.

Attempts to isolate the anilide of the diquinone failed on account of the uncrystallisable nature of the products.

Reduction of Dinaphtha-1 : 7 : 1′ : 7′-*diquinone*: 1 : 7 : 1′ : 7′-*Tetrahydroxydinaphthyl*, $C_{20}H_{10}(OH)_4$.

Freshly-prepared, moist amalgamated aluminium (made from aluminium wire) was added in portions of 2 grams to a solution of the diquinone (0·5 gram) in 50 c.c. of moist ether and 25 c.c. of acetone in a reflux apparatus. After two hours, when the originally yellow solution had become colourless, the filtered liquid was washed with a little water, dried over calcium chloride, and distilled to dryness under 100 mm. pressure, the drying being finally completed in a vacuum desiccator. The oily residue solidified to a pale yellow, semi-crystalline mass, which was dried on porous tile and washed with a little benzene to remove a brown impurity. The tetrahydroxydinaphthyl, thus obtained in almost theoretical yield, was crystallised from hot benzene or benzene-petroleum (b. p. 80—100°) in hard, yellowish-white, nodular crystals or from ether or acetone in small, slightly yellow, acicular prisms melting at 215—216° (Found: C = 75·80; H = 5·44. $C_{20}H_{14}O_4$ requires C = 75·45; H = 4·43 per cent.).

1 : 7 : 1′ : *7′-Tetrahydroxydinaphthyl* was readily soluble in alcohol, ether, or acetone. Unlike the diquinone, it showed no tendency to retain benzene of crystallisation. It gave no coloration with ferric chloride, and its solution in aqueous sodium hydroxide rapidly became reddish-purple on exposure to air.

The *tetra-acetyl* derivative, $C_{20}H_{10}(O{\cdot}CO{\cdot}CH_3)_4$, was obtained in quantitative yield by heating 1 : 7 : 1′ : 7′-tetrahydroxydinaphthyl with excess of acetic anhydride and anhydrous sodium acetate on the water-bath for one and a half hours; the solution was then evaporated to dryness in a vacuum desiccator, the residue washed with water, and the insoluble portion crystallised from benzene-petroleum, from which the compound separated in small, flattened, yellowish-white prisms melting at 188—189° (Found: C = 69·00; H = 5·11. $C_{28}H_{22}O_8$ requires C = 69·12; H = 4·56 per cent.).

The tetra-acetate was readily soluble in benzene, but less so in alcohol.

Reduction of Dinaphtha-1 : 7 : 1′ : *7′-diquinone with Hydriodic Acid.*

Twenty c.c. of 10 per cent. potassium iodide solution and 20 c.c. of dilute sulphuric acid (1 in 4 vols.) were added to an alcoholic solution (20 c.c.) of the diquinone (0·1109 gram). Iodine was liberated forthwith and titrated with *N*/10-sodium thiosulphate and starch-paper indicator, when 84·6 per cent. of the calculated amount was determined. The resulting solution was treated with excess of sodium acetate, concentrated under reduced pressure to half its bulk, and filtered from a green, flocculent material (quinhydrone ?) not melting below 300°. The ethereal extract of the filtrate furnished tetrahydroxydinaphthyl (yield 73 per cent.). Willstätter and Parnas found that with 2 : 6-naphthaquinone and hydriodic acid the iodine liberated and the 2 : 6-dihydroxynaphthalene produced were respectively 76 and 25 per cent. of the calculated amounts.

Reduction of the Diquinone with Heated Zinc Dust.

The diquinone (0·4 gram) mixed with 3 grams of zinc dust was distilled in a hard-glass tube through a layer of 10 grams of zinc dust, when an intensely yellow substance sublimed on to the cool part of the tube, accompanied by traces of naphthalene. The coloured product was odourless and sparingly soluble in ether or acetone to faintly blue fluorescent solutions. From these solvents it was obtained in minute, yellow needles melting at 238—239°. This substance, which still retained quinonoid characters, sublimed with difficulty and was very stable at temperatures above its melting point. On further heating with zinc dust, naphthalene was produced, but much of the substance sublimed unchanged. It was insoluble in aqueous sodium hydroxide, and gave a purple coloration with nitric acid. Lack of material has prevented a complete examination of this interesting product, the reactions of which would probably throw further light on the constitution of the diquinone.

We desire to express our grateful thanks to the Salters' Institute of Industrial Chemistry for the grant of a Fellowship to one of us (D.C.V.), which has rendered this collaboration possible.

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CXCVI.—*Chenopodium Oil.*

By THOMAS ANDERSON HENRY and HUMPHREY PAGET.

THE oil distilled from *Chenopodium ambrosioides* var. *anthelminticum* is now being used on a considerable scale in the campaigns against hookworm disease that are being carried on in various parts of the Tropics under the auspices of the International Health Board of the Rockefeller Foundation.

As a result of the investigations conducted by Kremers (*Pharm. Rev.*, 1907, **25**, 155), Schimmel & Co. (Bericht von Schimmel & Co., April, 1908, p. 109), and Nelson (*J. Amer. Chem. Soc.*, 1911, **33**, 1404; 1913, **35**, 84; 1914, **36**, 2521), it is known that the oil consists chiefly of a liquid organic peroxide, ascaridole, $C_{10}H_{16}O_2$, and a mixture of liquid hydrocarbons, of which until last year only one, cymene, had been identified with certainty. To account for the optical activity and a characteristic colour reaction of the hydrocarbon fraction, Schimmel & Co. suggested the presence of sylvestrene (*loc. cit.*), but this has received no support from later investigators (compare Wirth, *J. Amer. Pharm. Assoc.*, 1920, **9**, 139). Since the present authors began their work Nelson has re-examined the hydrocarbon fraction and produced evidence of the presence of α-terpinene and *l*-limonene (*J. Amer. Chem. Soc.*, 1920, **42**, 1204), whilst Caius and Mhaskar have stated, without adducing any experimental data, that the fraction contains cymene, terpinene, and phellandrene (*Ind. J. Med. Res.*, 1920, **7**, 570).

It has been assumed generally that the value of the oil as an anthelmintic is due to the ascaridole, but Hall and Hamilton have asserted as a result of an extensive series of pharmacological trials that the "lighter" portions (that is, the hydrocarbon fraction) are more active as anthelmintics than the "heavier" (ascaridole) fractions (*J. Pharm. Exp. Ther.*, 1918, **11**, 89). In view of this confusion, it seemed to the authors desirable that the oil should be re-examined and the nature and pharmacological action of its components definitely settled.

The pharmacological examination of the substances isolated from the oil has been undertaken by Dr. Wilson G. Smillie of the Instituto de Hygiene, San Paulo, Brazil, who has already obtained a number of interesting results, which will be recorded elsewhere.

EXPERIMENTAL.

Six lots of chenopodium oil, purchased through ordinary trade channels, were used. These had the following constants :

	(1)	(2)	(3)	(4)	(5)	(6)
d_{15}^{15}	0·9665	0·9663	0·9712	0·9723	0·9672	0·9582
Sp. rotation $[\alpha]_D^{15}$ ...	−5·7°	−4·5	−5·3°	−5·3°	−6·3°	−6·8°

The oils were separated by distillation under 15 mm. pressure into three fractions: (*a*) b. p. below 84°, d_{15}^{15} 0·8596 to 0·8839, $[\alpha]_D^{15^\circ}$ −14° to −18°; (*b*) b. p. 84—104°, d_{15}^{15} 0·9200 to 1·0070, $[\alpha]_D^{15^\circ}$ −5° to −11°; and (*c*) b. p. 104—118°, d_{15}^{15} 1·0120 to 1·0160, $[\alpha]_D^{15^\circ}$ −0·25° to −1·18°, which usually formed about 25, 15, and 55 per cent. respectively of the whole oil. The residual 5 per cent. is chiefly ascaridole glycol. The oil is difficult to fractionate, especially in the later stages, owing to the risk of explosive decomposition of the ascaridole. Fraction (*a*) consisted mainly of hydrocarbons, (*b*) of a mixture of hydrocarbons and ascaridole, and (*c*) was almost pure ascaridole. Fraction (*b*) was further treated by carefully heating it under a reflux condenser at atmospheric pressure, when the ascaridole decomposed with considerable violence, but without loss, giving the isomeric ascaridole glycol anhydride. On steam-distilling the product, the anhydride yielded the corresponding glycol, which was not volatile in steam, so that the distillate consisted almost wholly of hydrocarbons; this was added to fraction (*a*), which then formed about 30 per cent. of the whole oil.

Examination of the Hydrocarbon Fraction.

Acids.—On repeated agitation with 5 per cent. solution of sodium carbonate, the fraction yielded 0·9 per cent. of oily material having the characteristic odour of the lower fatty acids. This was converted into silver salts by neutralisation and precipitation in three portions with silver nitrate (Found: Ag = 56·27, 55·8, 57·6. Silver butyrate, $C_4H_7O_2Ag$, requires Ag = 55·4 per cent.).

Methyl Salicylate.—On further agitation of the fraction with 4 per cent. solution of sodium hydroxide, there was obtained on acidification 1·5 per cent. of a red oil, which on standing solidified in part, owing to the separation of salicylic acid (m. p. 156°), and the rest of the acid was removed by shaking the liquid portion with sodium carbonate solution. The liquid portion then boiled at 220°/755 mm., gave a benzoyl derivative, m. p. 83°, and was therefore methyl salicylate; the salicylic acid is no doubt formed by the action of the alkali on the ester during extraction.

As no evidence of the presence of other oxygenated compounds could be obtained, the mixture was then redistilled several times through a six-bulb Young dephlegmator, which separated it into three fractions boiling at 166—173°, 174—177°, and 177—180° under 765 mm. pressure. The middle fraction formed the bulk of the mixture, and this, on redistillation, was found to consist of a product having the following constants: b. p. 176·5—177°/765 mm.; d_{15}^{20} 0·8491; $[\alpha]_D^{20}$ −18·09°, n_D^{20} 1·48320. It had a slight lemon-like odour, and its solution in acetic anhydride gave a transient, bluish-red coloration with sulphuric acid. This product was prepared without difficulty from all six oils, and in spite of its constant boiling point was subsequently found to be a mixture of at least three hydrocarbons. The results of the analysis (Found: C = 88·14, 88·16, 88·63; H = 11·40, 11·10, 11·21) agree fairly well with those required for a mixture of terpenes, $C_{10}H_{16}$, with cymene, $C_{10}H_{14}$, in about equal proportions (namely, C = 88·9; H = 11·08 per cent.), and further evidence was obtained later of the presence of approximately this quantity of cymene.

Attempts to effect a further separation by distillation at different pressures through a twelve-bulb Young dephlegmator were unsuccessful.

Identification and Removal of α-Terpinene.—Further separation of the mixture by physical means having failed, recourse was had to the identification of the components and attempts to eliminate these in succession. On treatment with sodium nitrite in presence of acetic acid at 0°, the mixture gave a nitrosite, which, after recrystallisation from ethyl acetate, had m. p. 155° and showed no depression of melting point on admixture with α-terpinene nitrosite made from terpinene, prepared from either turpentine oil or terpineol. The formation of α-terpinene nitrosite had already been recorded by Nelson (*loc. cit.* Compare Caius and Mhaskar, *loc. cit.*), who, however, failed to obtain any other evidence of the presence of α-terpinene. Caius and Mhaskar state that phellandrene is also present. Phellandrene gives even in small quantities an excellent yield of a nitrosite of unmistakable appearance, and the present authors were unable to find any evidence of the formation of phellandrene nitrosite along with the α-terpinene derivative in the reaction.

Baeyer has shown (*Ber.*, 1894, **27**, 815) that small quantities of terpinene can be removed from its mixtures with other terpenes by repeated agitation in the cold with Beckmann's chromic acid mixture. Two hundred c.c. of the hydrocarbon fraction were treated repeatedly with small quantities of chromic acid mixture until no further absorption, and no increase in the specific rotation of the recovered oil, took place. The recovered oil, after distillation over sodium, had b. p. 176·5—177°/758 mm., $d^{23°}$ 0·8545, $[\alpha]_D^{15}$ —23·08°, n_D^{20} 1·48637 (Found: C = 89·08, 88·92, 88·80; H = 10·86, 10·59, 10·65. A mixture of terpene, $C_{10}H_{16}$, with cymene, $C_{10}H_{14}$, in the proportion of about 40 : 60 requires C = 89·04; H = 10·96 per cent.).

The recovered oil gave no crystalline nitrosite on treatment with sodium nitrite in acetic acid at 0°, but still gave the characteristic bluish-red coloration with sulphuric acid in presence of acetic anhydride, and on oxidation with potassium permanganate (see below) yielded no trace of the characteristic crystalline oxidation products of α-terpinene, whence it appears that the latter terpene had been completely eliminated by the treatment. The chromic acid mixture recovered yielded, on extraction with ether, a small quantity of a crystalline acid melting at 189°, which proved to be one of the forms of αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid produced by the oxidation of α-terpinene (see below).

Action of Bromine. Isolation of a New Terpene Tetrabromide.—Bromine, in excess of that required to form a tetrabromide, was added to either the original mixture of hydrocarbons or the α-terpinene-free mixture (see preceding paragraph) dissolved in its own volume of chloroform and cooled to 0°. After standing for one hour, the chloroform and excess of bromine were removed by a current of dry air, leaving a viscous, dark grey oil; this, on standing for six to eight weeks, deposited a solid tetrabromide, which after solution in ethyl acetate separated in large crystals up to about 1 gram in weight. The bulk of the brominated product remained liquid even after six months' exposure to a temperature of —15° to —20°, but on distillation under reduced pressure it yielded a considerable quantity of *p*-cymene (b. p. 175—176°), and the residue, on standing, then deposited a further quantity of the crystalline tetrabromide. The latter melted and decomposed at 117°, and repeated crystallisation from different solvents failed to change this melting point. Mixtures of equal parts of the tetrabromide with the tetrabromides of (*a*) *d*-limonene, m. p. 105°, (*b*) dipentene, m. p. 126°, (*c*) terpinolene, m. p. 112°, melted at (*a*) 90—95°, (*b*) 102—105°, (*c*) 100—104° respectively, so that the substance is not identical with any of the well-known terpene tetrabromides. The tetrabromide is optically inactive (Found: Br = 69·88, 70·08. $C_{10}H_{16}Br_4$ requires Br = 70·17 per cent.). It is apparently the formation of this substance on bromination that led Nelson (*loc. cit.*) to assume that the hydrocarbon fraction of chenopodium oil contained *l*-limonene. The tetrabromide of the latter, however, melts at 104—105°, is optically active ($[\alpha]_D = -73°$), and when crystallised with an equal quantity of *d*-limonene tetrabromide gives dipentene tetrabromide, m. p. 126°. In all these respects the new substance differs from *l*-limonene tetrabromide, and it is probably the tetrabromide of a new lævorotatory terpene.

The crystallographic examination of the new tetrabromide has been kindly undertaken for the authors by Dr. G. F. Herbert Smith of the Natural History Section of the British Museum, who reports as follows:

"The crystals are monoclinic. The prominent faces parallel to which the crystals are elongated belong to the form (110) and the faces observed at the end belong to the forms (001), (101), and ($\bar{1}11$). The fundamental data are $a:b:c = 1{\cdot}413:1:1{\cdot}471$; $\beta = 99° 51'$. The calculated and observed values of the biangular co-ordinates of the observed forms are given in the following table.

	Calculated.		Observed.	
Form.	ϕ.	ρ.	ϕ.	ρ.
110.................	—	—	0° 0′	35° 42′
$\bar{1}11$.................	48° 35′	42° 12′	48° 44′	41° 51′
101.................	—	—	39° 4′	90° 0′
001.................	—	—	80° 5′	90° 0′

"There is an optic axis very nearly perpendicular to the faces of the form (110) and the double refraction is high.

"The symmetry of the crystals is different from, and the measurements I have made do not harmonise at all with, those recorded by

Hintze for limonene tetrabromide (*Zeitsch. Kryst. Min.*, 1885, **10**, 252)."

No crystalline derivatives with halogen acids or nitrosyl chloride could be obtained from the mixture of hydrocarbons either before or after the removal of the α-terpinene. Sylvestrene yields a crystalline dihydrochloride.

Oxidation with Potassium Permanganate in Acetone. Isolation of p-*Cymene.*

The results recorded above indicate that the hydrocarbon fraction consists of α-terpinene, cymene, and a lævorotatory terpene, which forms an optically inactive, crystalline tetrabromide. It was hoped to obtain further information regarding this terpene by the oxidation of the whole hydrocarbon fraction with potassium permanganate in the cold, since the products of oxidation of α-terpinene under these conditions are well known and *p*-cymene is not attacked, so that any products of oxidation found other than those obtainable from α-terpinene might be assumed to come from the lævorotatory terpene. The oxidation was carried out in ice-cold water under the conditions prescribed by Wallach for α-terpinene (*Annalen*, 1908, **362**, 297), but it was subsequently found convenient to replace water by acetone. The hydrocarbon fraction (50 c.c.) was dissolved in acetone (150 c.c.) and a saturated solution of potassium permanganate in acetone added, 50 c.c. at a time, until the reagent was no longer decolorised immediately (*A*). After this stage, the oxidation proceeded very slowly and was completed by adding finely powdered permanganate with constant agitation until the liquid remained coloured for twenty-four hours after the last gram had been added (*B*); usually about 150 grams of permanganate were required in all. If the liquid is worked up at stage (*A*), 60 to 70 per cent. by volume of the oil originally used is recovered, and now has physical constants similar to those of the oil recovered after oxidation with cold chromic acid (p. 1717), with the exception that the highest specific rotation found was $-20°$ in place of $-23°$. It roughly corresponds, therefore, with the oxidation of the α-terpinene. The oil recovered at stage (*B*) was optically inactive, and after several distillations over sodium boiled constantly at 175—176°/763 mm., and had $n_D^{20°}$ 1·49041 (Found: $C = 89·2$, $89·3$; $H = 10·4$, $10·51$. *p*-Cymene, $C_{10}H_{14}$, requires $C = 89·57$; $H = 10·43$ per cent.). It yielded *p*-cymenesulphonic acid (Found: for the barium salt, $Ba = 24·4$. Calc., $Ba = 24·8$ per cent.), and on oxidation with aqueous potassium permanganate solution at 100° yielded *p*-hydroxy*iso*propylbenzoic acid, m. p. 153—154° (Found: $C = 66·45$; $H = 6·8$. Calc., C = 66·7; H = 6·7 per cent.), from which *iso*propenylbenzoic acid (m. p. 255°) was readily obtained by boiling with hydrochloric acid. The usual methods of identifying *p*-cymene are not very satisfactory. Many terpenes yield *p*-cymenesulphonic acid on treatment with sulphuric acid, and the authors have found that commercial phellandrene, on oxidation with hot permanganate, yields *p*-hydroxy*iso*propylbenzoic acid; special care was therefore taken in this case to prove that the recovered hydrocarbon was actually *p*-cymene. The amount recovered varied from 45 to 50 per cent. (compare p. 1716).

The products of oxidation were isolated by filtering off the manganese dioxide, distilling off the acetone, and steam-distilling the alkaline residue to recover the *p*-cymene. To the aqueous residue in the flask was added the aqueous extract obtained by suspending the manganese dioxide in water and passing through it a vigorous current of steam for two hours. The combined aqueous liquids were then reduced to low bulk in a vacuum and, when cold, extracted with ether, which removed a small amount of a viscous, neutral, yellow oil having a faint odour of mint. The liquid was then acidified and extracted repeatedly with ether, which removed a complex mixture of acids, mostly resinous, from which on standing there separated crystalline material (*A*) amounting to about 2 per cent. by weight of the oil originally used. When no more crystals would separate, the viscous acid resin was filtered off and steam-distilled. The acid distillate was neutralised with sodium hydroxide, evaporated to dryness, and mixed rapidly and completely with the quantity of sulphuric acid, cooled to −16°, required to convert the sodium into sulphate, which separated and was rapidly filtered off, leaving the volatile acids (*B*) as a dark brown liquid. The non-volatile residue in the flask was extracted with ether and yielded a large fraction of resinous acids (*C*).

Crystalline Acids (A).—A rapidly filtered solution in boiling water of the mixture of acids deposited, on standing, colourless, prismatic crystals, of which more was obtained by concentration of the mother-liquor in a vacuum. The crops were mixed and recrystallised from boiling water until of constant melting point, 203—204° (corr., decomp.). The acid was sparingly soluble in cold water or alcohol and less soluble in other solvents, and was optically inactive in aqueous solution (Found: C = 51·21, 51·12; H = 7·72, 7·82. $C_{10}H_{18}O_6$ requires C = 51·29; H = 7·69 per cent. Required for neutralisation, 8·57 c.c. of *N*-NaOH per gram. $C_8H_{16}O_2(CO_2H)_2$ requires 8·55 c.c. per gram).

The mother-liquor, on further concentration, deposited a second acid crystallising in rosettes of needles, which was recrystallised from water until the melting point remained constant at 189° (corr., decomp.). This substance was moderately soluble in water, and optically inactive in 5 per cent. aqueous solution (Found: C = 51·0, 51·26; H = 7·86, 7·79. $C_{10}H_{18}O_6$ requires C = 51·29; H = 7·69 per cent. Required for neutralisation, 8·56 c.c. of *N*-NaOH per gram. $C_8H_{16}O_2(CO_2H)_2$ requires 8·55 c.c. per gram).

These two acids appear to be identical with the two αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acids, $C_{10}H_{18}O_6$, obtained by Wallach by the oxidation of terpinen-4-ol from marjoram oil (*Annalen*, 1907, **356**, 212), which he describes as melting at 205—206° and 188—189° respectively. The acids decompose on melting and in the authors' experience the melting points can be varied from 203° to 214° and from 188° to 192° respectively by variation in the rate of heating. Wallach described the acid of higher melting point as the active and the other as the inactive acid, apparently because the latter only was produced by the oxidation of α-terpinene, which is itself optically inactive, whilst the active terpinenol from marjoram oil yielded both. The acid should, however, exist in more than one inactive modification, and both forms obtained by the present authors were inactive. It seemed likely that both these acids came from the α-terpinene, and this was confirmed by oxidising α-terpinene (prepared from terpineol) with permanganate in acetone, when the same two acids were obtained.

After the removal of the acid melting at 189°, concentration of the mother-liquor was continued, by slow evaporation at atmospheric temperature, causing the separation of a third substance, which, after several recrystallisations from water, melted at 179° (Found: C = 50·55, 50·84; H = 7·6, 7·69 per cent. Required for neutralisation, 8·38 c.c. of *N*-NaOH per gram). Mixed with either of the foregoing acids, this substance showed no depression in melting point, and it is probably merely a mixture of both.

Volatile Acids (B).—The dark brown, volatile acids isolated as already described (p. 1720) consisted mainly of acetic acid, since a series of eight fractions of silver salt prepared from them gave the following results: Ag = 62·5, 63·7, 64·4, 64·7, 65·1, 65·2, 65·3, 66·1. Silver acetate, $CH_3{\cdot}CO_2Ag$, requires Ag = 64·68 per cent. There is, however, present in addition a minute amount of an acid crystallising in long, slender needles, m. p. 117°, of which sufficient has not been obtained for examination; it can be isolated by steam-distilling the crude, volatile acids, stopping the distillation when the distillate begins to show only a weak acid reaction to litmus, and then extracting the residual liquor with ether.

Resinous Acids (C).—These form the bulk of the oxidation products and from them no definite substance has so far been obtained.

The only difference observed in the course of the oxidations with permanganate in (*a*) water and (*b*) acetone was that in the former case the volatile acids produced included *iso*butyric acid (Found: in the silver salt, Ag = 55·5, 55·7. Calc., Ag = 55·39 per cent.), which was separated from the acetic acid also formed by fractional crystallisation of the anilides, acetanilide, m. p. 114°, separating first from boiling water and *iso*butyranilide, m. p. 102°, last.

Oxidation with permanganate of the hydrocarbon fraction of chenopodium oil from which α-terpinene had been removed (p. 1717) yielded acetic and *iso*butyric acids and the volatile, crystalline acid melting at 117°. The latter appears, therefore, to be the only oxidation product found which may be characteristic of the lævorotatory terpene, and so far it has not been possible to obtain it in quantity sufficient for examination. From this terpinene-free fraction of the hydrocarbon mixture 58 per cent. of cymene was recovered on oxidation.

Oxidation of limonene and phellandrene, under the conditions described above, yielded none of the crystalline products obtained from the chenopodium mixture of hydrocarbons, thus confirming evidence already given of the absence of these terpenes from the mixture.

Ascaridole Fraction.

As already stated, fraction (*c*) consisted almost wholly of ascaridole and on redistillation had b. p. 108—110°/15 mm., $d^{15°}$ 1·0120, $[\alpha]_D^{15°}$ −0·5°, constants which are in good agreement with those already on record (Found: C = 71·63; H = 9·45. Calc., C = 71·43; H = 9·53 per cent.). As stated above, ascaridole, when heated above 160°, is converted explosively into an isomeric substance, ascaridole glycol anhydride, the temperature rising to about 300°. Nelson found that the action could be readily controlled by dropping ascaridole into cymene heated at 150°. The authors found that dilution of ascaridole with any volatile, indifferent solvent boiling at about 130—150°, for example, xylene, will serve equally well. After the reaction is complete, the solvent is distilled off, leaving a residue of the anhydride which can be purified by distillation. It forms a viscous, yellow oil, b. p. 230—245°/755 mm., 122—125°/20 mm.; d^{15} 1·026; $[\alpha]_D^{15°}$ −0·72°.

By treatment with steam, the anhydride is converted into ascaridole glycol, which is not volatile in steam, but can be distilled apparently unchanged under reduced pressure. Obtained in this way, it is a heavy, green, viscous oil, b. p. 135—160°/15 mm. (Found: C = 64·55; H = 9·74. Calc., C = 64·46; H = 9·74 per cent.). It was previously prepared by Nelson (*loc. cit.*) by shaking ascaridole with ferrous sulphate solution or by hydrating the anhydride by dilute sulphuric acid. The monobenzoate melts at 136—137°, as recorded by Nelson (Found: C = 70·68; H = 7·92. Calc., C = 70·34; H = 7·55 per cent.).

Indian Chenopodium Oil.

In connexion with attempts made in recent years to cultivate chenopodium in India for the production of oil, two samples of the drug have been received from Col. A. T. Gage, Director of the Botanical Survey of India. These were labelled *C. ambrosioides* and *C. anthelminticum* and yielded 0·17 and 0·24 per cent. of oil having d^{15}_{15} 0·9399, $[\alpha]^{15}_{D}$ + 0·07°, and d^{15}_{15} 0·9080, $[\alpha]^{15}_{D}$ −9·6° respectively. The quantities obtained were too small for further investigation.

Summary of Results.

1. Chenopodium oil contains minute quantities of the lower fatty acids, chiefly butyric acid, and less than 0·5 per cent. of methyl salicylate. The remainder of the oil consists of at least 60 per cent. of ascaridole with about 5 per cent. of the corresponding glycol and 30 to 40 per cent. of a mixture of hydrocarbons made up approximately of cymene 15 per cent., α-terpinene 5 per cent., and a new lævorotatory terpene, 10 per cent. No evidence has been obtained of the presence in the oil of sylvestrene, limonene, phellandrene, safrole, or camphor, all of which have been suggested or recorded as constituents.

2. The lævorotatory terpene has not been isolated from the mixture of hydrocarbons, but judging from the physical constants of its mixtures with (*a*) α-terpinene and cymene, and (*b*) cymene alone, it must have approximately the following characters: b. p. 177—178°/760 mm., d^{15° 0·847, $[\alpha]^{15^\circ}_{D}$ −57°, n^{20}_{D} 1·484. It furnishes a well-crystallised tetrabromide, m. p. 117°, which is optically inactive, and on oxidation with permanganate yields acetic and *iso*butyric acids and possibly a volatile, crystalline acid, m. p. 117°, not yet identified. It is interesting to note that Lewinsohn (*Arch. Pharm.*, 1906, **244**, 424) isolated from myrrh oil a terpene having the following constants; b. p. 78—80°/20 mm., d^{20° 0·847, $[\alpha]^{20^\circ}_{D}$ + 80°, yielding a tetrabromide, m. p. 115°.

3. On oxidation with permanganate in acetone, α-terpinene yields two forms of αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid melting at 203—204° and 189° respectively; the latter has already been obtained by Wallach by oxidation of this terpene with permanganate in water at 0°, and both acids by the same author from the terpinen-4-ol of marjoram oil by the same means. The acid of higher m. p.

is described by Wallach as active, although no determination of the value is given; both acids obtained by the present authors were optically inactive in aqueous solution.

The authors desire to express their cordial thanks to Dr. Herbert Smith for the crystallographic measurements recorded above and to Mr. F. Walton for assistance in the experimental work.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

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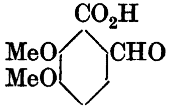
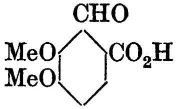
CXCVII.—m-*Opianic Acid* (4 : 5-*Dimethoxy*-o-*aldehydobenzoic Acid*).

By ROBERT GEORGE FARGHER and WILLIAM HENRY PERKIN, jun.

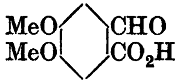
THE opianic acids (dimethoxy-*o*-aldehydobenzoic acids),



Opianic acid (m. p. 150°) *from narcotine.*



ψ-Opianic acid (m. p. 121°) *from berberine.*

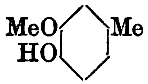


m-*Opianic acid (m. p.* 185°) *from cryptopine.*

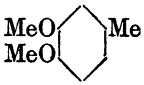
have so far only been obtained from alkaloids either by direct oxidation or by the oxidation of their degradation products.

In view of the importance of these acids, it is curious that there should be no record of any attempt having been made to prepare them synthetically. It seemed therefore interesting to devise methods for the synthesis of these acids and the present communication contains an account of the steps which have led to the synthesis of *m*-opianic acid.* It is hoped that it may, in the near future, be found possible to synthesise opianic acid and *ψ*-opianic acid as well and thus to complete the series.

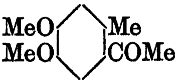
The starting point in the synthesis of *m*-opianic acid is creosol (I), which is first methylated by means of methyl sulphate; the resulting homoveratrole (II) is then converted by the action of acetyl chloride in the presence of aluminium chloride into 4 : 5-dimethoxy-*o*-tolyl methyl ketone (III)



(I.)



(II.)



(III.)

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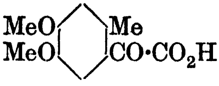
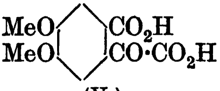
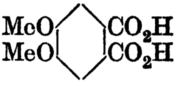
* The name *m*-opianic acid was given to this acid because it is the opianic acid corresponding with *m*-hemipinic acid.

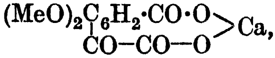
(compare Harding and Weizmann, T., 1910, **97**, 1126). When this ketone is oxidised by permanganate, it yields 4 : 5-dimethoxy-*o*-tolylglyoxylic acid (IV), 4 : 5-dimethoxyphthalonic acid (V), and *m*-hemipinic acid (VI).


(IV.)


(V.)


(VI.)

4 : 5-Dimethoxyphthalonic acid (V) was first obtained by Perkin (T., 1902, **81**, 1022) during the investigation of the oxidation of trimethylbrazilin by means of permanganate, and was stated to melt at 150°. Subsequently Harding and Weizmann (*loc. cit.*, p. 1129) prepared the same acid * from 4 : 5-dimethoxy-*o*-tolyl methyl ketone by oxidation with permanganate, and these investigators found that a specimen of the acid dried in the steam-oven melted at 148°. These observations are incorrect, and the reason for the inaccuracy is to be found in the facts (i) that the acid, like phthalonic acid itself, has no definite melting point, and (ii) that the indefinite melting point is lowered by traces of moisture and slight impurity to an unusual degree.

We have, on several occasions, repeated the preparation of 4 : 5-dimethoxyphthalonic acid under the conditions recommended by Harding and Weizmann, and have always obtained an acid which crystallised well from water and melted roughly at 145—150°. It was then found that the acid prepared in this way invariably contains traces of oxalic acid, which apparently cannot be removed by recrystallisation, and the purification by means of the calcium salt, recommended in this case and in the case of the acid from trimethylbrazilin, is of no avail, since both acids yield calcium salts which are insoluble in water. Subsequently the observation was made that the insoluble *neutral* calcium salt of 4 : 5-dimethoxyphthalonic acid,  $\left.\begin{matrix}(MeO)_2C_6H_2\cdot CO\cdot O \\ CO-CO-O\end{matrix}\right>Ca$, is converted by the calculated amount of dilute hydrochloric acid into a beautifully crystalline, soluble *acid* calcium salt, $(C_{11}H_9O_7)_2Ca$, whereas calcium oxalate remains unchanged, and this observation has made it possible to prepare the phthalonic acid readily in a state of purity.

4 : 5-Dimethoxyphthalonic acid crystallises from water in prisms usually of the composition $C_{11}H_{10}O_7,2H_2O$, and does not melt completely until 188° (compare p. 1736). When it is heated in the steam-oven, it loses one molecule of water, but the other is not lost at 120°, and does not seem to be removable by heat without

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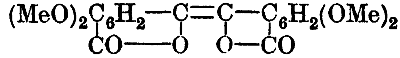
* Called by them 6-carboxy-3 : 4-dimethoxyphenylglyoxylic acid.

decomposition of the acid. It is therefore probable that the formula of the hydrated acid, crystallised from water and dried at 100°, is $(MeO)_2C_6H_2(CO_2H)\cdot C(OH)_2\cdot CO_2H$. On the other hand, the acid is somewhat soluble in dry ether and, after digesting with anhydrous sodium sulphate and concentrating, it separates in colourless prisms which are anhydrous and have the formula $C_{11}H_{10}O_7$.

This acid now crystallises from water in *anhydrous* prisms, and it seems possible that the hydrated acid is derived from V, whereas the anhydrous acid has the constitution XVII. This interesting point is being investigated.

When 4 : 5-dimethoxyphthalonic acid is heated at 200—210°, it is completely decomposed, with the formation mainly of *m*-hemipinic acid, but small quantities of the anhydride of *m*-opianic acid (p. 1742) are produced, as well as traces of a substance melting above 260°, which appears to be *tetramethoxydiphthalyl*,



$$\begin{array}{l}(MeO)_2C_6H_2{-}C{=}C{-}C_6H_2(OMe)_2 \\ \qquad\ \ CO{-\!\!-}O\quad O{-}CO\end{array},$$

and to be identical with the substance, $C_{20}H_{16}O_8$, which had previously been obtained (Perkin, T., 1902, **81**, 1025) from the same acid by heating with water in a sealed tube at 200°. In this behaviour, dimethoxyphthalonic acid resembles phthalonic acid itself, which, on heating, is decomposed into phthalic anhydride, phthalaldehydic acid, and diphthalyl (Graebe and Trümpy, *Ber.*, 1898, **31**, 371). When 4 : 5-dimethoxyphthalonic acid is heated with concentrated sulphuric acid on the steam-bath, it is decomposed, apparently quantitatively, into carbon monoxide and *m*-hemipinic acid.

The conversion of 4 : 5-dimethoxyphthalonic acid into m-*opianic acid* has been carried out in two different ways :

(i) *By Heating with Sodium Hydrogen Sulphite.*—In this case the sodium hydrogen sulphite derivative of the phthalonic acid, which is first produced, is decomposed by heating on the steam-bath into carbon dioxide and the corresponding derivative of *m*-opianic acid. When the latter is treated with hydrochloric acid and the product extracted with ether, *m*-opianic acid crystallises from the ether in a state of purity.

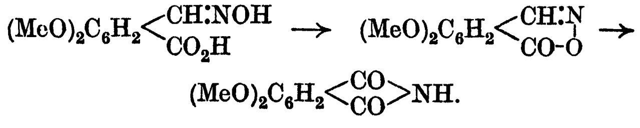
(ii) *With the Aid of Aniline or* p-*Toluidine* (p. 1740).—Aniline reacts very readily with a hot aqueous solution of 4 : 5-dimethoxyphthalonic acid with separation of a crystalline substance (m. p. 179—180°) which is the *aniline* salt of *anilino*-4 : 5-*dimethoxyphthalonic acid* and probably has the formula

$$(MeO)_2C_6H_2(CO_2H)\cdot C(:N\cdot C_6H_5)\cdot CO_2H,C_6H_5\cdot NH_2.$$

When this is boiled with xylene, it loses carbon dioxide and the substance which crystallises from the xylene and melts at 213—214°, is *anilino*-m-*opianic acid*, $(MeO)_2C_6H_2{<}\genfrac{}{}{0pt}{}{CH(NH\cdot C_6H_5)}{CO\text{———————}}{>}O$ (compare p. 1738). Warm dilute hydrochloric acid readily hydrolyses this anilino-derivative with formation of aniline hydrochloride and *m*-opianic acid, and as the decomposition is quantitative and the acid crystallises direct in an almost pure state from the hydrochloric acid, this is much the most convenient method for the preparation of *m*-opianic acid. In the case of *p*-toluidine, the course of the different reactions is similar. The substance first produced is the p-*toluidine* salt of p-*toluidino*-4 : 5-*dimethoxyphthalonic acid*, and this, on boiling with xylene, yields p-*toluidino*-m-*opianic acid* (m. p. 223°), from which *m*-opianic acid is obtained by hydrolysis with dilute hydrochloric acid. There is not much to choose between the aniline and *p*-toluidine processes, but the latter was preferred and employed for the preparation of most of the *m*-opianic acid required for this investigation.

m-Opianic acid melts at 186—187° or considerably higher than either opianic acid (m. p. 150°) or ψ-opianic acid (m. p. 121°); like opianic acid, it is very sparingly soluble in cold water and indeed in nearly all its properties and reactions it resembles opianic acid very closely. Some of the more characteristic derivatives of *m*-opianic acid were prepared from the specimen of this acid which was originally obtained by the oxidation of cryptopidene (T., 1916, **109**, 929), and these are the following:

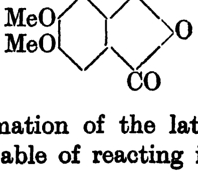
The oxime (m. p. 140°) and the oxime anhydride (m. p. 132—133°), both of which on heating pass into *m*-hemipinimide:



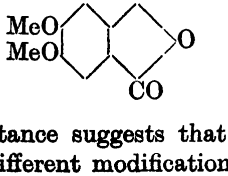
$$(MeO)_2C_6H_2{<}\genfrac{}{}{0pt}{}{CH\colon NOH}{CO_2H} \longrightarrow (MeO)_2C_6H_2{<}\genfrac{}{}{0pt}{}{CH\colon N}{CO\text{-}O} \longrightarrow (MeO)_2C_6H_2{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}NH.$$

The semicarbazone, $(MeO)_2C_6H_2(CO_2H)\cdot CH\colon N\cdot NH\cdot CO\cdot NH_2$, melts at 227°.

m-Opianic acid was also reduced to *m*-meconine and yielded, on acetylation, acetyl-*m*-opianic acid (m. p. 159°).



and



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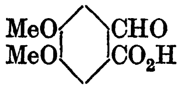
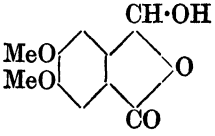
The formation of the latter substance suggests that *m*-opianic acid is capable of reacting in two different modifications, namely, as the *normal* acid (VII) and as the *pseudo*-acid or derivative of hydroxyphthalide (VIII),



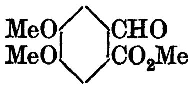
(VII.)



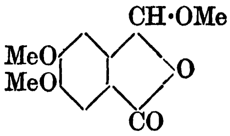
(VIII.)

and much new material has now been accumulated which shows clearly how very closely opianic acid and *m*-opianic acid resemble each other in this respect. One of the most characteristic properties of opianic acid is that of yielding two series of esters, namely, the *normal* carboxylic esters and the *pseudo*-esters derived from the hydroxyphthalide formula and containing the grouping >CH(OMe).

An exactly similar property is exhibited by *m*-opianic acid. When the silver salt of this acid is digested with methyl iodide, the methyl ester formed is the *normal* ester (IX; m. p. 95°), but the *pseudo*-methyl ester (X; m. p. 143°) is produced when *m*-opianic acid is boiled with methyl alcohol.



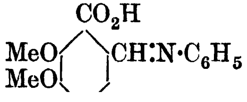
(IX.)



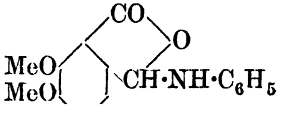
(X.)

In cases other than that of the isomeric esters, opianic acid yields derivatives both of the *normal* and *pseudo*-modification.

Towards semicarbazide, this acid behaves as the aldehyde, but Liebermann (*Ber.*, 1896, **29**, 174) has shown that the action of aniline and other amino-compounds on the acid results in the formation of crystalline substances which are always derivatives of the *pseudo*-modification. Thus the anilino-derivative (m. p. 187°) is insoluble in cold dilute sodium carbonate and cannot therefore be the normal derivative (XI), but must have the constitution represented by (XII).



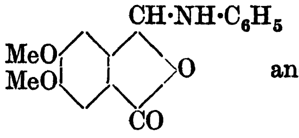
(XI.)



(XII.)

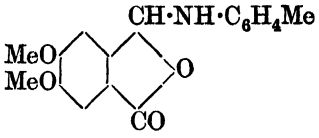
A careful investigation has shown that *m*-opianic acid behaves in these respects exactly like opianic acid. The semicarbazone of *m*-opianic acid is evidently derived from the normal acid, because it is immediately soluble in cold sodium carbonate solution. Aniline and *p*-toluidine react very readily with aqueous or alcoholic solutions of *m*-opianic acid, yielding immediate, crystalline precipitates of the anilino- and *p*-toluidino-derivatives, which melt at 213° and 222° respectively and are insoluble in cold dilute sodium carbonate solution.

The constitutions of these substances must therefore be represented by the formulæ:



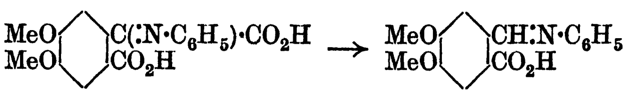
(XIII.)

and



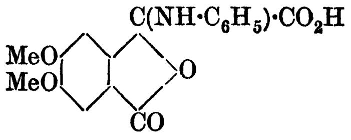
(XIV.)

It is remarkable that the substance (m. p. 213°) produced by the action of aniline on *m*-opianic acid should prove to be identical with that which results when the anilino-derivative of 4 : 5-dimethoxyphthalonic acid is heated with xylene (p. 1727). It is clear that the change

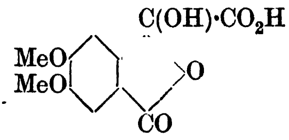


(XV.)

does not accurately represent the decomposition, and it must therefore be assumed either that formula XV undergoes molecular change into XIII or that the anilino-derivative of the phthalonic acid has the constitution XVI.



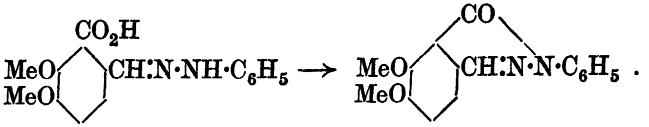
(XVI.)



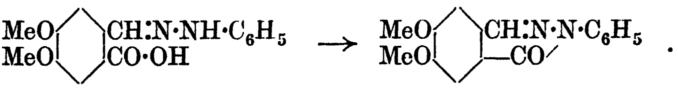
(XVII.)

It is also, of course, possible that the phthalonic acid itself is capable of reacting in the pseudo-form XVII, in which case the anilino-derivative would be XVI and its conversion into XIII as the result of loss of carbon dioxide would follow as a matter of course.

In one respect, opianic acid and *m*-opianic acid exhibit a striking and unexpected difference, and that is in their behaviour with phenylhydrazine. When a warm aqueous solution of opianic acid is mixed with phenylhydrazine, it yields an oily, yellow *hydrazone* which very rapidly becomes crystalline owing to the conversion into *phenylopiazone* (m. p. 175°; p. 1744):



In the case of *m*-opianic acid, the yellow, crystalline *hydrazone* (XVIII) is remarkably stable, and may indeed be crystallised from methyl alcohol. At 185—190°, however, it becomes colourless owing to the formation of *phenyl*-m-*opiazone* (XIX) (m. p. 228°; p. 1743):



(XVIII.) (XIX.)

Both opianic and *m*-opianic acids react with *as*-phenylmethylhydrazine to produce stable derivatives of the formula

$$(MeO)_2C_6H_2(CO_2H){\cdot}CH{:}N{\cdot}NMe{\cdot}C_6H_5$$

(m. p. 167° and 237° respectively), which, owing to the presence of the *N*-methyl group, are incapable of yielding derivatives of the type phenylopiazone.

EXPERIMENTAL.

Homoveratrole (Formula II).

Homoveratrole was first obtained by Tiemann and Mendelsohn (*Ber.*, 1875, **8**, 1137) by the action of methyl iodide on the potassium derivative of creosol [$CH_3{\cdot}C_6H_3(OMe){\cdot}OH = 1:3:4$], and later (T., 1906, **89**, 1649) Perkin and Weizmann simplified the process by substituting methyl sulphate for the methyl iodide.* In preparing the large quantities of material required for the present investigation, the following method was found to work well. The solution of creosol (50 grams) in methyl alcohol (150 c.c.) was gradually mixed with methyl sulphate (60 c.c.) and methyl-alcoholic potassium hydroxide (180 c.c. of 25 per cent.), and so soon as the reaction had subsided the whole was heated on the steam-bath for a few minutes, cooled, diluted with water, rendered strongly alkaline by the addition of sodium hydroxide, and extracted with ether. The extract was dried over potassium carbonate, the ether removed, and the residue fractionated, when about 45 grams of homoveratrole distilled at 128—130°/25 mm. and some unchanged creosol was recovered from the alkaline liquors.

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* There is an error in the quantities given for the preparation of veratrole from catechol; the amount of methyl sulphate should be 275 grams, and not 75 grams.

It was noticed that homoveratrole, after standing in the ice-chest for some days, had solidified to a mass of striated prisms; after purification by partial melting and decantation of the melted portion, the crystals melted at about 22°.

4 : 5-*Dimethoxy*-o-*tolyl Methyl Ketone* (Formula III).

Harding and Weizmann (T., 1910, **97**, 1127) obtained this substance by acting on homoveratrole and acetyl chloride, dissolved in carbon disulphide, with aluminium chloride, but we have obtained a larger yield and a purer product by allowing the aluminium chloride to react first with the acetyl chloride and afterwards adding the homoveratrole.

Freshly-prepared and finely-powdered aluminium chloride (100 grams) is gradually added to the well-cooled solution of acetyl chloride (30 grams) in carbon disulphide (200 c.c.) and, after standing for half an hour, homoveratrole (50 grams) is slowly run in, with constant stirring and cooling in ice-water. After remaining over-night, the mixture is heated on the steam-bath until hydrogen chloride ceases to be evolved, the carbon disulphide removed by distillation, and the residue decomposed by much powdered ice. The product is extracted with ether, the ethereal solution well washed with dilute hydrochloric acid and repeatedly shaken with 5 per cent. sodium hydroxide so long as the extract (A) is brown; it is then dried over calcium chloride, concentrated to a small bulk, and left in the ice-chest, when a crust of prisms quickly separates. The mother-liquor is decanted and the crystals are washed with a little ether with suction; the substance then melts at 76—77°, and consists of pure 4 : 5-dimethoxy-*o*-tolyl methyl ketone.

The ethereal filtrate is evaporated and the residue fractionated under reduced pressure, when, after traces of homoveratrole have passed over, the whole distils at 175°/15 mm. and crystallises on cooling.

The ketone is rather sparingly soluble in cold methyl alcohol, but dissolves very readily on warming, and separates, when slowly cooled, in large, almost colourless, glistening prisms which do not lend themselves to accurate crystallographical measurement. The yield is about equal to the amount of homoveratrole employed in the synthesis.

The *oxime* was obtained by boiling the ketone (1·4 grams) with hydroxylamine hydrochloride (1 gram) in alcoholic solution in the presence of excess of sodium acetate. Water was added, when, on standing, the oxime separated in colourless prisms which, after recrystallisation from water, melted at 138° (Found : N=6·8. $C_{11}H_{15}O_3N$ requires N = 6·7 per cent.).

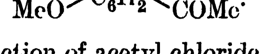
The semicarbazone was prepared by boiling the ketone (1 gram) with semicarbazide hydrochloride (1·2 grams) and sodium acetate (3 grams) in aqueous alcohol for half an hour. On cooling, the semicarbazone separated, and was recrystallised from alcohol, when it melted at 208°. Harding and Weizmann (*loc. cit.*, p. 1128) state that it decomposes at 186° (Found : N = 16·8. Calc., N = 16·7 per cent.).

The phenylhydrazone separated gradually in crystals when the ketone was heated on the steam-bath with phenylhydrazine in dilute acetic acid solution. It was collected with the aid of the pump and washed with methyl alcohol, in which it was sparingly soluble. The colourless, crystalline residue melted without decomposition at 182°, whereas Harding and Weizmann (*loc. cit.*, p. 1128) state that this phenylhydrazone melts at 168—170° with decomposition (Found : N = 10·5. Calc., N = 10·4 per cent.).

The *benzylidene* derivative, $(MeO)_2C_6H_2Me\cdot CO\cdot CH{:}CH\cdot C_6H_5$, separated as a mass of crystals when the solution of the ketone and benzaldehyde in a small quantity of methyl alcohol was mixed with a few drops of 50 per cent. potassium hydroxide and allowed to stand. After crystallisation from alcohol, from which it separated in needles, it melted at 110° (Found : C = 76·8; H = 6·5. $C_{18}H_{18}O_3$ requires C = 76·6; H = 6·4 per cent.).

The *piperonylidene* derivative, prepared in a similar manner, crystallises from alcohol and melts at 109°.

5-Hydroxy-4-methoxy-o-tolyl Methyl Ketone,



$$\begin{matrix}OH\\MeO\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}Me\\COMe\end{matrix}.$$

This substance, produced during the interaction of acetyl chloride with homoveratrole in the presence of aluminium chloride, is extracted from the main product of the reaction with sodium hydroxide (A, p. 1731).

The deep brown, alkaline extract is acidified, when an oil separates which soon solidifies to a brown mass; this is collected, washed, and extracted several times with boiling water. The aqueous extract, after decolorising with animal charcoal, deposits a mass of glistening crystals, and a further considerable crop is obtained by concentrating the filtrate on the steam-bath under reduced pressure. Finally, the substance is crystallised either from much light petroleum or from a mixture of benzene and light petroleum, in which it is more soluble, and from which it separates in colourless, glistening, fern-like masses (Found: C = 66·3; H = 6·8. $C_{10}H_{12}O_3$ requires C = 66·6; H = 6·7 per cent.). A Zeisel determination gave OMe = 16·7, whereas $C_{10}H_{12}O_3$ containing 1OMe requires OMe = 17·2 per cent.

5-*Hydroxy*-4-*methoxy*-o-*tolyl methyl ketone* melts at 123° and is sparingly soluble in water or light petroleum, but dissolves readily in methyl alcohol or benzene. The solution in methyl alcohol gives with ferric chloride a rather faint yellowish-green coloration.

The *phenylhydrazone* was prepared by adding the hydroxy-ketone (1 gram) to a solution of phenylhydrazine (3 grams) in 50 per cent. acetic acid and heating on the steam-bath for a few minutes. The yellow solution clouded on cooling and gradually deposited the hydrazone as a crystalline mass, which was collected and recrystallised from methyl alcohol, in which it was sparingly soluble in the cold and from which it separated in glistening prisms melting at 164—165° (Found: N = 10·4. $C_{16}H_{18}O_2N_2$ requires N = 10·4 per cent.).

The Semicarbazone.—The hydroxy-ketone dissolves in a hot strong solution of semicarbazide acetate and, on standing, groups of prisms slowly separate. This semicarbazone softens at 220° and decomposes at about 228—230°; it is sparingly soluble even in boiling water, but dissolves readily in dilute sodium hydroxide solution (Found: N = 17·7. $C_{11}H_{15}O_3N_3$ requires N = 17·7 per cent.).

The *piperonylidene* derivative,

$$MeO{\cdot}C_6H_2Me(OH){\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2,$$

is readily prepared by boiling the hydroxy-ketone with a methyl-alcoholic solution of piperonal and rather more than one molecular proportion of potassium hydroxide for twenty minutes. After most of the methyl alcohol has been distilled off under reduced pressure, dilute hydrochloric acid is added, and the solid mass crystallised from alcohol, from which it separates in yellow needles melting at 158° (Found: C = 69·0; H = 5·2. $C_{18}H_{16}O_5$ requires C = 69·2; H = 5·2 per cent.).

The Acetyl Derivative.—In preparing this derivative, the hydroxy-ketone was boiled with excess of acetyl chloride for half an hour and the excess distilled from the clear solution, when a syrup remained which soon crystallised. The whole was stirred with a little methyl alcohol, in which the acetyl derivative was sparingly soluble, filtered with the aid of the pump, and recrystallised from methyl alcohol, from which the acetyl derivative separated in prismatic needles melting at 108° (Found: C = 64·8; H = 6·5 $C_{12}H_{14}O_4$ requires C = 64·8; H = 6·3 per cent.).

Methylation of the Hydroxy-ketone.—The ketone (1 gram), suspended in a little methyl alcohol, was gradually mixed with methyl sulphate (1·5 c.c.) and methyl-alcoholic potassium hydroxide (5 c.c. of 25 per cent.), and, after remaining for an hour, the whole was heated on the steam-bath for ten minutes. On the addition of water, a mass of needles gradually separated, and this was collected and recrystallised from a little methyl alcohol, from which the substance separated in small prisms melting at 76°. That this substance is 4 : 5-dimethoxy-*o*-tolyl methyl ketone (m. p. 76—77°; p. 1731) was shown by careful comparison and by the method of mixed melting points. The conversion under the conditions described above is almost quantitative.

Oxidation of 4 : 5-*Dimethoxy*-o-*tolyl Methyl Ketone.*

The main object of the study of this oxidation was to discover the conditions for the preparation of 4 : 5-dimethoxy-*o*-phthalonic acid in a state of purity. It is explained in the introduction (p. 1725) that the oxidation of this ketone by means of permanganate leads to the formation, not only of the acid just mentioned, but also of 4 : 5-dimethoxy-*o*-tolylglyoxylic acid, *m*-hemipinic acid, and oxalic acid, and the complete separation of the phthalonic acid from oxalic acid proved to be particularly difficult. As the result of a series of comparative experiments, the following process has now been devised, which yields the phthalonic acid without difficulty in a state of purity. A flask containing water (200 c.c.), potassium carbonate (10 grams), and the ketone (20 grams), and fitted with a vigorously acting stirrer, is heated on the steam-bath until the ketone has melted, the source of heat is then removed, and a solution of potassium permanganate (75 grams) in boiling water (800 c.c.) run in rather rapidly. The oxidation appears to take place in distinct stages, the first probably being the oxidation of the acetyl group and the second that of the methyl group. At first the permanganate is very rapidly reduced, sufficient heat being developed to cause the liquid to boil vigorously; at the second stage, the action is much less rapid and the flask may be replaced on the steam-bath to complete the action.

The whole is filtered with the aid of the pump, and the faintly coloured filtrate and washings of the manganese precipitate are mixed with hydrochloric acid until the yellow colour produced just persists; the liquid is now acid to litmus, but does not react with Congo-paper. After concentrating considerably on the steam-bath, the hot liquid, which is now acid to Congo-paper, is made strongly alkaline with ammonia, mixed with calcium chloride

(40 grams) dissolved in a little water, and, while still hot, the granular precipitate is collected with the aid of the pump and washed with hot water (filtrate B). The residue, a mixture of the calcium salt of the phthalonic acid and calcium oxalate, is stirred with hot water and dilute hydrochloric acid until the liquid is just (but distinctly) acid to Congo-paper. In this way the insoluble neutral calcium salt of the phthalonic acid is converted into the soluble acid salt, whereas the calcium oxalate remains unchanged.

After filtering from the calcium oxalate, the filtrate is evaporated to a small bulk, when, on standing, the *acid calcium* salt separates splendidly as a hard crust of prisms; it is collected (C) and allowed to dry in the air. Analysis showed that this salt, dried at 100°, is anhydrous [Found : Ca = 7·5. $(C_{11}H_{10}O_6)_2Ca$ requires Ca = 7·3 per cent.].

This salt is rather readily soluble in boiling water, but sparingly so in the cold, and when the hot solution is decomposed with a considerable excess of hydrochloric acid (the phthalonic acid is much less soluble in hydrochloric acid than in water), the solution gradually deposits the pure acid in crusts of pale amber prisms. A large crop of crystals of the same acid is also obtained when the filtrate from the calcium salt (C) is mixed with excess of hydrochloric acid and allowed to stand. The filtrate (B) from the neutral calcium salts is concentrated considerably, when, on standing, a crust of calcium salt separates. This salt is very sparingly soluble in boiling water, but readily so in hot dilute hydrochloric acid, and, on cooling, an acid separates in pale ochre *needles* which melt at 202—204° with vigorous effervescence, and this was found to be *m*-hemipinic acid.* On mixing the filtrate from the calcium salt of this acid with a large excess of hydrochloric acid, a turbidity was produced and soon a large quantity of a crystalline acid separated which, after recrystallisation from hot water, melted at 155° and proved to be 4 : 5-dimethoxy-*o*-tolylglyoxylic acid, $(MeO)_2C_6H_2Me\cdot CO\cdot CO_2H$ (Harding and Weizmann, T., 1910, **97**, 1128).

After working up the mother-liquors, the yields of the various substances obtained from the product of the oxidation of 60 grams of 4 : 5-dimethoxy-*o*-tolyl methyl ketone were as follows :

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* (Found: C = 53·2; H = 4·5. $C_{10}H_{10}O_6$ requires C = 53·1; H = 4·4 per cent.). At certain concentrations, *m*-hemipinic acid separates in groups of *prisms* without water of crystallisation, and, if rapidly heated, these melt at 189—190° with vigorous decomposition (compare Dobbie and Lauder, T., 1899, **75**, 677). The behaviour of the acid with ammoniacal calcium chloride is characteristic. If the strongly alkaline solution of the ammonium salt is mixed with calcium chloride, there is no immediate precipitate, but the solution will soon gelatinise, and, on boiling, the sparingly soluble calcium salt separates in a crystalline form.

4 : 5-Dimethoxyphthalonic acid	40 grams
4 : 5-Dimethoxy-*o*-tolylglyoxylic acid	16 „
m-Hemipinic acid	1·5 „
Calcium oxalate	4·5 „

If the oxidation had proceeded completely from the ketone to the phthalonic acid, the yield of the latter should have been about 80 grams.

4 : 5-*Dimethoxyphthalonic Acid* (Formula V).

This acid is almost miscible with boiling water, and the pale amber prisms which separate on cooling contain two molecules of water, since, on analysis, the air-dry substance gave C = 45·8, 45·7; H = 5·0, 5·1, whereas $C_{11}H_{10}O_7,2H_2O$ requires C = 45·6; H = 4·9 per cent. When the crystals are heated in the steam-oven, they readily lose 1 mol. of water (Found : loss = 6·7. $C_{11}H_{10}O_7,2H_2O$, losing $1H_2O$, requires loss = 6·3 per cent.) and the acid then gave C = 48·6; H = 4·6, whereas $C_{11}H_{10}O_7,H_2O$ requires C = 48·5; H = 4·4 per cent.

There is no further loss on heating at 120°, indicating that the remaining molecule of water is constitutional.* The acid has no definite melting point. If the crystals containing $2H_2O$ are rapidly heated in a capillary tube, they soften at 100°, become yellow, and are partly melted at 150°, but fusion is not complete until 187°, when decomposition takes place with evolution of gas (see below) and formation of a yellow syrup. After the hydrated acid has been thoroughly dried in the steam-oven, there is no softening below 150°, but above this temperature the acid becomes yellow, gradually softens, and melts at 188° with decomposition.

It was subsequently found possible to prepare the unhydrated phthalonic acid by digesting the hydrated acid with much ether, in which it is very sparingly soluble, and anhydrous sodium sulphate on the steam-bath for two hours. After remaining for two days with frequent shaking, the ethereal solution was concentrated considerably, when, on standing, a crust of colourless prisms separated (Found : C = 52·0; H = 4·0. $C_{11}H_{10}O_7$ requires C = 52·0; H = 3·9 per cent.).

This specimen of anhydrous 4 : 5-dimethoxyphthalonic acid softened and became gradually yellow above 170° and melted at about 187° with decomposition. It is curious that the anhydrous acid is sparingly soluble in cold water and dissolves only gradually on warming, whereas the hydrated acid is very readily soluble in water (see p. 1726).

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* The statement (T., 1902, **81**, 1023) that this acid loses two molecules of water at 100° is incorrect.

Decomposition by Heat.—If the crystals, $C_{11}H_{10}O_7,2H_2O$, are heated in a test-tube at 200—210° in a sulphuric acid bath, the melted mass becomes yellow, gives off water and a little carbon dioxide, but the gas does not burn, and no direct experiment has been made to demonstrate the presence of carbon monoxide. A small sublimate, probably consisting of tetramethoxydiphthalyl (p. 1726), is deposited in yellow needles on the portion of the tube actually in the hot sulphuric acid.

The yellowish-brown melt, which solidified completely, was boiled with a considerable volume of water, when a cloudy liquid was produced which, on cooling, deposited a small quantity of a red-ochreous mass. This was collected (A) and recrystallised from glacial acetic acid, in which the substance was very sparingly soluble and from which it separated in pale yellow crystals melting above 250°. This substance is probably identical with the substance, $C_{20}H_{16}O_8$, previously obtained (Perkin, T., 1902, **81**, 1025) by heating 4 : 5-dimethoxyphthalonic acid with water in a sealed tube at 200°, and there can be little doubt that it is tetramethoxydiphthalyl (compare p. 1726). It dissolves in concentrated sulphuric acid, yielding an intense purple solution, and the addition of a drop of nitric acid changes the colour to deep bluish-violet. The aqueous filtrate (A) from this substance was concentrated considerably, when it deposited a very small quantity of the anhydride of *m*-opianic acid in needles melting at 230°. On remaining exposed to the air, the filtered solution gradually deposited pale amber prisms, which melted at 188—190° and consisted of *m*-hemipinic acid, and this acid is the main product of the decomposition. It was curious that the mother-liquor from this acid, on long standing, gradually deposited a small quantity of the much less soluble *m*-opianic acid.

Action of Sulphuric Acid.—4 : 5-Dimethoxyphthalonic acid is coloured orange-red by sulphuric acid, and, on warming in the steam-bath, the solution becomes deep reddish-brown and effervesces owing to the escape of carbon monoxide. On diluting with water, the colour is discharged and the liquid sets to a mass of crystals of *m*-hemipinic acid which, in this case, separated from water in needles melting at 200—202°.

Action of Aniline on 4 : 5-*Dimethoxyphthalonic Acid. Formation of the Aniline Salt of Anilino*-4 : 5-*dimethoxyphthalonic Acid,* $(MeO)_2C_6H_2(CO_2H)\cdot C(:N\cdot C_6H_5)\cdot CO_2H,C_6H_5\cdot NH_2$.

The hot aqueous solution of 4 : 5-dimethoxyphthalonic acid (2·5 grams) reacts readily with aniline (3 c.c.), and if the cloudy liquid is kept at 80—90°, a mass of crystals of the above aniline salt will soon separate.

This is collected with the aid of the pump and washed well with water and then with benzene, which removes all the coloured impurity and leaves the pure aniline salt as a colourless, crystalline mass melting with vigorous decomposition at 179—180°. The yield is about 1·8 grams (Found : C = 65·4 ; H = 5·4 ; N = 6·4. $C_{23}H_{22}O_6N_2$ requires C = 65·4 ; H = 5·2 ; N = 6·6 per cent.). This substance is rather sparingly soluble in methyl alcohol in the cold, but dissolves readily on boiling and separates in glistening laminæ. It is almost insoluble in benzene or light petroleum, and rather sparingly so in cold acetone, from which, however, it crystallises well. It dissolves in hot glacial acetic acid, but nothing separates on cooling or diluting with water. Dilute hydrochloric acid colours it yellow, and on warming a clear, colourless solution results, from which nothing separates on cooling.

The crystals of the aniline salt dissolve readily in concentrated sulphuric acid to a deep orange-red solution.

The aniline salt is decomposed by cold sodium hydroxide solution with the separation of aniline, and it is interesting, as showing the great tendency to form this salt, that if the liquid is now rendered faintly acid with hydrochloric acid, the aniline salt again separates, melting at 178° (Found : N = 6·2 per cent.). If, however, the aniline is removed from the alkaline solution by extraction with ether, hydrochloric acid precipitates a viscous acid which gradually sets to a resin, and this substance is presumably anilino-4 : 5-dimethoxyphthalonic acid, but it was not further investigated.

The aniline salt decomposes on heating at 180—190° with elimination of carbon dioxide, and the residual resin crystallises from methyl alcohol, melts at about 190° to a cloudy syrup, and consists of slightly impure anilino-*m*-opianic acid (see below).

This substance was subsequently prepared in considerable quantity in the following way. The aniline salt (2 grams) is almost insoluble in pure xylene (20 c.c.), but, on boiling in a reflux apparatus for half an hour, carbon dioxide is eliminated and a clear yellow solution obtained. On cooling, a mass of crystals separates, and these are collected and boiled with much methyl alcohol in order to separate the anilino-derivative from a very sparingly soluble substance present in small quantity (A, see p. 1740).

From the concentrated filtrate, the new substance separates as a meal of short prisms (Found: N = 5·0. $C_{16}H_{15}O_4N$ requires N = 4·9 per cent.).

Anilino-m-*opianic acid* (formula XIII) melts at 213—214° and is very sparingly soluble even in boiling methyl alcohol; it dissolves more readily in acetone and crystallises well in short prisms. It is coloured yellow by concentrated hydrochloric acid and dissolves in concentrated sulphuric acid, yielding a deep pure yellow solution which, on the addition of a drop of nitric acid, changes to intense brown. It is soluble in dilute ammonia in the cold to a colourless solution. The decomposition of this substance by hot dilute hydrochloric acid into aniline hydrochloride and *m*-opianic acid is described on p. 1740.

Action of p-*Toluidine on* 4 : 5-*Dimethoxyphthalonic Acid*.—The solution of the acid (2·5 grams) in boiling water (25 c.c.) was mixed with *p*-toluidine (3·5 grams) and the whole heated on the steam-bath, when a crystalline substance separated which was collected with the aid of the pump and washed first with water and then with light petroleum. The colourless residue of the p-*toluidine* salt of p-*toluidino*-4 : 5-*dimethoxyphthalonic acid* (compare p. 1727) separates from methyl alcohol in glistening flakes and decomposes, with evolution of gas, at 163—165° (Found: N = 6·3. $C_{25}H_{26}O_6N_2$ requires N = 6·2 per cent.). When this substance (3 grams) was boiled in a reflux apparatus with xylene (12 c.c.) for half an hour, crystals of p-*toluidino*-m-*opianic acid* (formula XIV) began to separate from the hot liquid. After cooling, the substance was collected and washed with benzene, when it melted at about 223° (Found: N = 4·7. $C_{17}H_{17}O_4N$ requires N = 4·7 per cent.).

This substance is decomposed on boiling with dilute hydrochloric acid in a similar manner to the corresponding anilino-derivative, yielding *p*-toluidine hydrochloride and *m*-opianic acid.

m-*Opianic Acid* (4 : 5-*Dimethoxy*-o-*aldehydobenzoic Acid*) (Formula VII).

This acid may be obtained from 4 : 5-dimethoxyphthalonic acid (i) by boiling with a solution of sodium hydrogen sulphite, or (ii) by digesting anilino-*m*-opianic acid (see above) with dilute hydrochloric acid.

In process (i), the phthalonic acid (25 grams), dissolved in water and mixed with anhydrous sodium carbonate (11 grams), is evaporated to dryness, when the sodium salt remains as a satiny, crystalline mass. Freshly-prepared sodium hydrogen sulphite (100 c.c. of 50 per cent.) is warmed at 50°, the powdered sodium salt gradually added, and the whole heated in a water-bath at 60° for half an hour and then on the steam-bath until gas ceases to be evolved. The mass is evaporated to a paste, mixed with a large excess of 10 per cent. hydrochloric acid, evaporated to complete dryness, and extracted with ether in a Soxhlet apparatus for ten days, during which nearly pure *m*-opianic acid separates from the ether in crusts. The drawbacks to this process are the tedious ether extraction and the fact that the yield is not more than 60 per cent. of that theoretically possible.

In process (ii), crude anilino-*m*-opianic acid (as it separates from the xylene, p. 1738), in quantities of 10 grams, is heated on the steam-bath with water (50 c.c.) and concentrated hydrochloric acid (20 c.c.), when the yellow colour first produced soon fades and partial solution takes place. After half an hour, the whole is cooled, the precipitated acid collected, washed with a little water, warmed with dilute sodium carbonate solution, and filtered from a small quantity of an insoluble substance (A).* On acidifying the filtrate with hydrochloric acid, a chalky precipitate separates which melts at 184—185° and consists of almost pure *m*-opianic acid.

After recrystallisation from water, in which the acid is very sparingly soluble in the cold and from which it separates as a chalky powder consisting of microscopic, fern-like groups of needles, the melting point was 186—187° (Found: $C = 57{\cdot}2$; $H = 5{\cdot}0$. $C_{10}H_{10}O_5$ requires $C = 57{\cdot}1$; $H = 4{\cdot}8$ per cent.). *m*-Opianic acid is very sparingly soluble even in boiling methyl alcohol, but dissolves readily in boiling acetone; it is also readily soluble in glacial acetic acid and separates in microscopic balls of needles. It crystallises particularly well from 50 per cent. acetic acid in rather characteristic stars of long, striated needles. A careful comparison showed that this acid is identical with the *m*-opianic acid (m. p. 184—185°) obtained from cryptopidene by oxidation with permanganate (T., 1916, **109**, 928). In addition to the properties recorded at that time, the following observations have been made. A mixture of the acid with phenol gives, with a little concentrated sulphuric acid, a pale cherry-red coloration which, on warming, becomes deeper and then brown. Water precipitates a yellowish-green substance which dissolves in sodium hydroxide to a cherry-red solution. The acid, suspended in benzene containing thiophen, gives with sulphuric acid an intense cherry-red coloration which disappears on dilution with water. The acid dissolves in sulphuric acid to a yellow solution, which gradually becomes brown; at 160°, much sulphur dioxide is disengaged and the colour becomes deep green and then violet. On adding water, a brown substance separates which dissolves in sodium hydroxide, producing a deep violet solution, evidently due to the presence of an anthraquinone derivative corresponding with rufiopin (tetrahydroxyanthraquinone), which is formed under similar conditions from opianic acid (Liebermann and Chojnacki, *Annalen*, 1872, **162**, 323).

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* This curious substance is almost insoluble in the ordinary organic solvents, but crystallises from much boiling glacial acetic acid in lemon-yellow spangles which do not melt at 280° (Found: $C = 66{\cdot}3, 66{\cdot}0$; $H = 5{\cdot}2, 5{\cdot}3$; $N = 4{\cdot}3, 4{\cdot}5$. $C_{16}H_{15}O_4N$ requires $C = 67{\cdot}4$; $H = 5{\cdot}3$; $N = 4{\cdot}9$ per cent.). This substance is insoluble in boiling methyl-alcoholic potassium hydroxide, but dissolves readily in concentrated sulphuric acid without change of colour, and the addition of water gives a gelatinous precipitate.

The Methyl Esters of m-*Opianic Acid* (compare p. 1728).

The *normal methyl* ester (formula IX) is obtained when methyl iodide reacts with the silver salt of *m*-opianic acid.

This silver salt was precipitated, on the addition of excess of silver nitrate to the neutral solution of the ammonium salt of *m*-opianic acid, as a gelatinous mass which, on standing and especially on warming, became granular and crystalline. It was collected with the aid of the pump, washed well, and dried on porous porcelain in the steam-oven (Found: Ag = 34·0. $C_{10}H_9O_5Ag$ requires Ag = 34·0 per cent.).

The dry salt was powdered, digested with anhydrous ether and excess of methyl iodide in a reflux apparatus for two hours, and the ethereal solution evaporated, when a colourless syrup remained which gradually crystallised in warty groups; crystallisation was much facilitated by rubbing with a little methyl alcohol. After draining on porous porcelain, the substance was recrystallised from methyl alcohol, in which it was much more readily soluble than the *pseudo*-methyl ester (see below) (Found: C = 58·7; H = 5·2. $C_{11}H_{12}O_5$ requires C = 58·9; H = 5·3 per cent.).

This *normal methyl* ester of m-*opianic acid* melts at 93—95° and is readily soluble in benzene and most organic solvents, but is sparingly soluble in light petroleum. It is insoluble in cold dilute sodium hydroxide, but dissolves readily on warming, and hydrochloric acid gives a precipitate of *m*-opianic acid melting at 185°.

Action of Aniline.—When aniline is added to the warm solution of the normal methyl ester in methyl alcohol, the clear liquid soon begins to deposit a colourless, crystalline substance which melts at about 143° (Found: N = 4·8. $C_{17}H_{17}O_4N$ requires N = 4·7 per cent.).

There can be no doubt that this interesting substance is the methyl ester of normal anilino-*m*-opianic acid,

$$(MeO)_2C_6H_2(CO_2Me)\cdot\dot{C}H\!:\!N\cdot C_6H_5.$$

The *pseudo-methyl* ester of m-*opianic acid* (formula X) is produced when *m*-opianic acid (2·5 grams) is boiled with methyl alcohol (50 c.c.) in a reflux apparatus for two hours. The product is concentrated to a third of its bulk, when, on standing, the *pseudo*-methyl ester (2·2 grams) separates as a mass of colourless needles (Found: C = 59·0; H = 5·3. $C_{11}H_{12}O_5$ requires C = 58·9; H = 5·3 per cent.).

This pseudo-methyl ester melts at 142—143° and is less soluble in organic solvents than the normal methyl ester. It dissolves, however, readily in benzene, but is almost insoluble in light petroleum, and crystallises well from a mixture of benzene and a little light petroleum in needles. It does not dissolve in dilute methyl-alcoholic potassium hydroxide in the cold, but, on boiling, is at once converted into the sparingly soluble potassium salt of *m*-opianic acid. It differs from the normal methyl ester in crystallising unchanged from hot methyl alcohol to which aniline has been added.

Anhydride of m-*Opianic Acid.*

This substance is readily produced when the acid, contained in a test-tube, is heated in a sulphuric acid bath for four hours at 200° and then for two hours at 230°. The residue is pale brown and sets to a transparent mass like colophony, which is almost insoluble in water or dilute ammonia.

It was powdered, dissolved in boiling acetone, the solution digested with animal charcoal, and concentrated, when, on cooling, a voluminous mass of colourless needles separated (Found: C = 59·5; H = 4·5. $C_{20}H_{18}O_9$ requires C = 59·7; H = 4·5 per cent.).

This anhydride shrinks at 210° and melts at about 230°; it is sparingly soluble in cold methyl alcohol or acetic acid, but dissolves very readily in boiling acetone. It crystallises well from acetic acid as a voluminous mass of needles. It does not dissolve in methyl-alcoholic potassium hydroxide in the cold, but does so readily on warming and, after adding water and boiling away the methyl alcohol, the addition of hydrochloric acid gives a clear solution, from which *m*-opianic acid crystallises in needles melting at 185°.

Action of Aniline on m-*Opianic Acid.*

When the boiling aqueous solution of the acid is mixed with aniline, a cloudy liquid is produced and soon a mass of crystals will separate. The same substance is obtained when aniline is added to a boiling methyl-alcoholic solution of *m*-opianic acid. It is sparingly soluble in boiling methyl alcohol and crystallises in stout prisms melting at 213—214°.

An analysis, careful comparison, and mixed melting-point determination showed that this substance is identical with the anilino-*m*-opianic acid obtained in the manner described on p. 1727. As this result was unexpected (compare p. 1729), a similar experiment was made on the action of *p*-toluidine on *m*-opianic acid, when a substance was immediately produced which, after crystallisation from methyl alcohol, melted at 220—222° and was found to be identical with the *p*-toluidino-*m*-opianic acid described on p. 1727.

Action of Phenylhydrazine on m-*Opianic Acid: Formation of the Phenylhydrazone of* m-*Opianic Acid and of Phenyl*-m-*opiazone* (Formulæ XVIII and XIX).

When phenylhydrazine is added to the boiling aqueous solution of *m*-opianic acid, a voluminous, crystalline precipitate separates which, since it is completely soluble in cold dilute ammonia, evidently consists entirely of the phenylhydrazone and does not contain any phenyl-*m*-opiazone (see below). This substance is very sparingly soluble in boiling methyl alcohol, and separates in minute, lemon-yellow needles which must be at once collected, because, if allowed to remain, they will become contaminated with colourless crystals of *phenyl*-m-*opiazone* (Found: N = 9·2. $C_{16}H_{16}O_4N_2$ requires N = 9·3 per cent.). The hydrazone shows a striking behaviour in a capillary tube, since at 185—190° the yellow crystals suddenly become colourless owing to conversion into phenyl-*m*-opiazone and the melting point is then 228°. Another way of converting the hydrazone into the opiazone is by boiling with concentrated hydrochloric acid, when the orange solution first produced becomes colourless and crystals of the opiazone separate. This substance was recrystallised from much alcohol, from which it separated in glistening needles melting at 228° (Found: N = 9·8. $C_{16}H_{14}O_3N_2$ requires N = 9·9 per cent.).

Phenyl-m-*opiazone* dissolves in concentrated sulphuric acid to a colourless solution, and the addition of a drop of nitric acid produces a salmon coloration which is discharged by water.

Action of as-*Phenylmethylhydrazine.*—When the boiling aqueous solution of *m*-opianic acid is mixed with phenylmethylhydrazine, a voluminous, crystalline precipitate separates which crystallises from alcohol, in which it is very sparingly soluble, in balls of yellow needles (Found: N = 9·1. $C_{17}H_{18}O_4N_2$ requires N = 8·9 per cent.). The *phenylmethylhydrazone* of m-*opianic acid* melts at about 237° without change of colour, and is incapable, owing to the presence of the methyl group, of being converted into a substance of the type of phenyl-*m*-opiazone. When heated at 250°, this substance melts to a dark brown syrup, gives off gas, and the residue crystallises in needles insoluble in ammonia. No further examination was, however, made of this product.

Action of Phenylhydrazine and of Phenylmethylhydrazine on Opianic Acid.

These experiments were instituted with the object of comparing the behaviour of opianic acid and *m*-opianic acid when treated with these reagents. Liebermann (*Ber.*, 1886, **19**, 764) states that the hot aqueous solution of opianic acid gives, with phenylhydrazine hydrochloride and sodium acetate, an oil which, on cooling, solidifies and after recrystallisation melts at 175° and has the formula $C_{16}H_{14}O_3N_2$ (phenylopiazone). Since this behaviour is very different from that of *m*-opianic acid (see above), the action of phenylhydrazine on opianic acid was repeated and it was found that the oil produced on mixing a hot aqueous solution of opianic acid with phenylhydrazine is evidently the normal phenylhydrazone, $C_{16}H_{16}O_4N_2$, since it is completely soluble in ammonia in the cold. This substance, unlike the phenylhydrazone of *m*-opianic acid, is very unstable and quickly passes into phenylopiazone with loss of water. The stable phenylmethylhydrazone is readily obtained when a boiling aqueous solution of opianic acid (5 grams) is mixed with phenylmethylhydrazine (2·5 c.c.). The milky liquid deposits an oil which will soon crystallise, and this substance separates from methyl alcohol, in which it is readily soluble, in groups of lemon-yellow needles (Found: $N = 8{\cdot}9$. $C_{17}H_{18}O_4N_2$ requires $N = 8{\cdot}8$ per cent.).

Opianic acid phenylmethylhydrazone melts at 167° with previous softening, and is immediately soluble in cold dilute ammonia.

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CXCVIII.—*The Constitution of Polysaccharides. Part III. The Relationship of* l-*Glucosan to* d-*Glucose and to Cellulose.*

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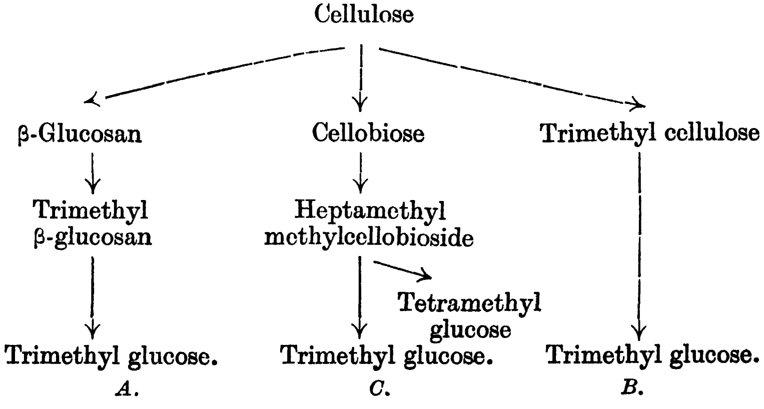
IN a previous communication (Irvine and Soutar, T., 1920, **117**, 1489) it has been shown that the yield of pure glucose obtainable from cotton cellulose is, as a minimum, 85 per cent. of the theoretical amount calculated on the basis of the equation $(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6$. This result is in itself insufficient to prove that the molecular unit of unmodified cellulose consists entirely of condensed glucose residues, but additional evidence pointing to this conclusion has been obtained in the course of recent work (Monier-Williams, this vol., p. 803). During the past four years, discussion on the constitution of cellulose has been prominent, and of the various structural alternatives which have been put forward the simplest is that cellulose may be regarded as a polymeride of $C_6H_{10}O_5$. The unit, in turn, would be derived from glucose, so that, on this basis, the degradation of cellulose involves both depolymerisation and hydrolysis. It is unnecessary to review the earlier literature in which this idea has been developed, as the subject has been extensively studied by Pictet and his collaborators, who, in a series of papers, have contributed some interesting suggestions (Pictet and Sarasin, *Helv. Chim. Acta*, 1918, **1**, 187, and subsequent papers).

It will be recalled that, by subjecting either cellulose or starch to dry distillation under diminished pressure, Pictet obtained a number of volatile products, the most significant being the well-defined crystalline compound hitherto known as "*l*-glucosan." The compound in question, which had previously been obtained by the hydrolysis of certain natural glucosides, possesses the formula $C_6H_{10}O_5$ and is convertible into glucose on treatment with acids. Glucosan thus represents one of the possible anhydro-glucoses, and it may be remarked that according to current views on sugar structure (Irvine, Fyfe, and Hogg, T., 1915, **107**, 524, and subsequent papers) no fewer than forty non-reducing anhydro-glucoses may exist, and the number of isomerides is increased to 100 if reducing compounds are taken into account. Pictet's observation is interesting and offers a convenient method of preparing glucosan, but it is doubtful if the formation of this anhydride gives any clue to the constitution of starch or of cellulose. According to Pictet, both polysaccharides are polymerides of glucosan, and consequently dry distillation involves merely disruption of the complexes into the simple units of which they are composed. In the particular case of carbohydrates, where the complexity of the changes undergone during heating are notorious, it is unlikely that clear evidence as to molecular structure could be obtained in any reaction conducted at high temperatures. Nevertheless Pictet, in extending his experiments on the dry distillation of carbohydrates and their derivatives, has not only claimed that cellulose and starch are polymerides of glucosan, but has not hesitated to propose radical alterations in the formulæ generally accepted for certain natural glucosides, the suggestions being based on the fact that, in such cases also, glucosan was present in the volatile products of decomposition. These conclusions will be criticised in due course, meanwhile it may be stated that the results now communicated show that there is no structural relationship between cellulose and *l*-glucosan. It is inadvisable to speculate as to the course of the reactions involved in the dry distillation of cellulose, but, as acids are produced, it is highly probable that hydrolysis to β-glucose is an essential factor and that the sugar is thereafter converted into the corresponding anhydride. It has, in fact, been proved experimentally in the course of the present research that *l*-glucosan is 1 : 6-β-glucose anhydride and accordingly the expression "β-glucosan" may be substituted for the older name.

In order to explain the principle underlying the investigation, it is necessary to refer to results obtained in this laboratory by Denham and Woodhouse (T., 1913, **103**, 1735, and subsequent papers). These workers found that cellulose could be converted into a trimethyl cellulose from which, on hydrolysis, a crystalline trimethyl glucose was obtained. Obviously, if cellulose is a polymerised β-glucosan, trimethyl cellulose must be regarded as a polymeride of trimethyl β-glucosan. Pictet's views can thus be subjected to a rigid experimental test by preparing trimethyl glucosan and converting it into the corresponding trimethyl glucose by hydrolysis. The scheme involved, together with the relationship of cellulose to cellobiose, may be represented diagrammatically as under:



If the trimethyl glucoses indexed as *A* and *B* are identical, it follows that the glucosan unit is present in cellulose, and Pictet's polymerisation theory would then receive strong support. On the other hand, if the methylated glucoses are isomeric, Pictet's views cannot be upheld. We find that the trimethyl glucose (*A*) derived from glucosan is not identical with that prepared from trimethyl cellulose, but is the sugar already obtained by one of us from methylglucoside (Irvine and Dick, T., 1919, **115**, 593) and by Haworth and Leitch (T., 1919, **115**, 809) from maltose. Further, the identity of *B* and *C* (Haworth and Hirst, this vol., p. 193) shows clearly that the cellobiose residue is an integral part of the cellulose molecule.

β-Glucosan, prepared by Pictet's method, was converted by the silver oxide reaction into trimethyl β-glucosan, at least two treatments with the methylating mixture being necessary. Unless properly conducted, excessive oxidation occurred with the consequent formation of alkylated acids and esters, but under suitable conditions a good yield of trimethyl glucosan was obtained. This compound distilled at 135°/12 mm. as a mobile, refractive liquid which solidified to a mass of large, colourless prisms, melting after recrystallisation from ethyl acetate or from ether at 63—64°. The compound is readily soluble in organic solvents, is lævorotatory, and is devoid of action upon Fehling's solution.

When trimethyl β-glucosan was heated at 100° with dilute hydrochloric acid, the rotation altered from lævo to dextro, and the trimethyl glucose thus produced was isolated as described in the experimental part. The properties of the sugar are compared below with those of the isomeride obtained from trimethyl cellulose.

Trimethyl glucose from glucosan.	*Trimethyl glucose from trimethyl cellulose.*
Liquid; b. p. 160—164°/0·2 mm.	Crystalline; m. p. 123—124°.
Gives trimethyl glucosan on heating.	Stable on heating.
Gives a crystalline β-methylglucoside.	Gives a liquid β-methylglucoside.
May be obtained from maltose but not from cellobiose.	May be obtained from cellobiose but not from maltose.

Despite the fact that their optical rotations lie close together, there can be no doubt that the compounds are utterly distinct, and the significance of this result has already been pointed out.

With the object of establishing the constitution of glucosan, attention was accordingly directed to the detailed study of the trimethyl glucose obtained from it. The variable optical rotations displayed by different preparations of the sugar suggested its identity with the form of trimethyl glucose already isolated from methylglucoside and from maltose.

Trimethyl Glucose.

	(1) From methyl-glucoside.	(2) From maltose.	(3) From β-glucosan.
$[\alpha]_D$ in water	+ 48·6°; 60·7°	+ 60·3°	+ 47·3°; 66·8°
,, in acetone	+ 46·2°; 58·8°	+ 61·4°	+ 60·8°
n_D	1·4780 1·4768	1·4792	1·4780; 1·4789
Composition found	C = 49·03; H = 7·98	C = 48·52; H = 8·02	C = 48·58; H = 8·09 %

Composition calculated ... C = 48·64; H = 8·10 %

It will be seen that although the five different preparations of the sugar proved on oxidation to be identical in structure, the specific rotations showed curious irregularities. A satisfactory explanation of this is found in the analytical results, in which the hydrogen value is slightly low whilst the carbon content is either very close to the calculated value or is actually higher. We have shown that the variations in activity and the abnormality in the analytical results are due to the tendency of the sugar to pass into the corresponding anhydride, small quantities of which are produced in the course of vacuum distillation. This internal dehydration takes place most readily with the β-isomeride and the production of even minute quantities of the β-anhydride (that is, trimethyl glucosan) depresses the activity greatly without notable alteration of the analytical results.

The most trustworthy optical rotation of the trimethyl glucose is given by observing the end-point attained when the sugar is formed by hydrolysis. Thus, on hydrolysing trimethyl glucosan, the specific rotation of the sugar present in the solution was +75·8°, whilst starting from trimethyl methylglucoside the value +73·8° was recorded. The true rotation of the sugar in water is doubtless of the above order, but the identification of this form of trimethyl glucose is a difficult matter and depends ultimately on the results of oxidation.

In the first place, in order to establish that the trimethyl glucose obtained from glucosan is a derivative of butylene-oxide glucose, the compound was fully methylated by the silver oxide reaction. The product consisted of α- and β-tetramethyl methylglucosides which, on hydrolysis, were converted into tetramethyl glucose of the butylene-oxide type, melting, after recrystallisation, at 95—96°.*

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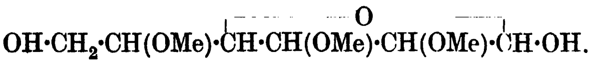
* It is unfortunately necessary to correct one of the misleading statements made by Karrer, who has chosen to conduct investigations on the field associated with this laboratory and to copy our methods. He claims (Karrer

When oxidised with nitric acid, the trimethyl glucose was converted into trimethyl saccharolactone, which was isolated in the form of its ethyl ester. From this, in turn, the parent lactonic acid was regenerated and found to be identical with that described by Haworth and Leitch (*loc. cit.*). The compound is thus derived from a dibasic acid, and the trimethyl glucose yielding such an acid must have the constitution shown below :



$$\mathrm{OH{\cdot}CH_2{\cdot}CH(OMe){\cdot}\overbrace{CH{\cdot}CH(OMe){\cdot}CH(OMe){\cdot}CH}^{O}{\cdot}OH.}$$

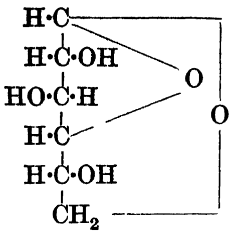
As a necessary consequence, it follows that in the formation of glucosan from glucose, dehydration involves the reducing group and also the terminal primary alcoholic group. Provided the butylene-oxide structure is preserved (which has now been shown to be the case), two possibilities are available according as the sugar reacts in its α- or β-form. There should thus be two possible glucosans possessing the following constitution :

and Widmer, *Helv. Chim. Acta*, 1921, **4**, 174) that "β-tetramethyl glucose" melts at 94°, and not at the lower values which have been reported in our papers. It may be pointed out that although many researches have been devoted to the subject, β-tetramethyl glucose is quite unknown, as only the α-form and the equilibrium mixture have been isolated. Evidently Karrer has made the elementary mistake of assuming that a sugar isolated from a β-glucoside will permanently retain the β-configuration.

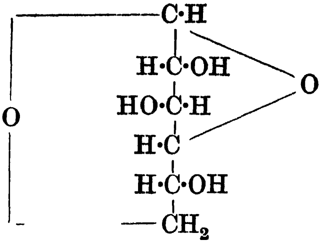
That Karrer's statement is not due to a typographical error is confirmed by the importance he attaches to the fact that, in the complete methylation of cellobiose, he obtained a pure β-form, whereas Haworth and Hirst's preparation of heptamethyl methylcellobioside (*loc. cit.*) admittedly contained some of the α-isomeride. This implied criticism of Haworth and Hirst's results is quite unjustified, as, irrespective of the proportions of α- and β-forms in a glucoside, the same sugar is isolated after hydrolysis. This was established many years ago (Purdie and Irvine, T., 1904, **85**, 1049, and subsequent papers) as part of the pioneer work conducted in this laboratory in preparation for our investigation of the constitutional problems of the di- and poly-saccharides.

The error made by Karrer is unlikely to mislead experienced workers in the sugar group, but unless corrected may give rise to confusion in view of the complications of the nomenclature now in use.

Further, it must be stated that it has long been known to us that the melting point of tetramethyl glucose rises as the content of the α-isomeride increases. The melting point thus varies greatly according to the proportion of α-form present and is further affected, owing to conversion into the β-isomeride, by the rate of heating during the determination. Values of 100° may be obtained by rapid heating, but we prefer to quote an average figure based, not on one result, but on an experience extending over twenty years.



α-Glucosan.

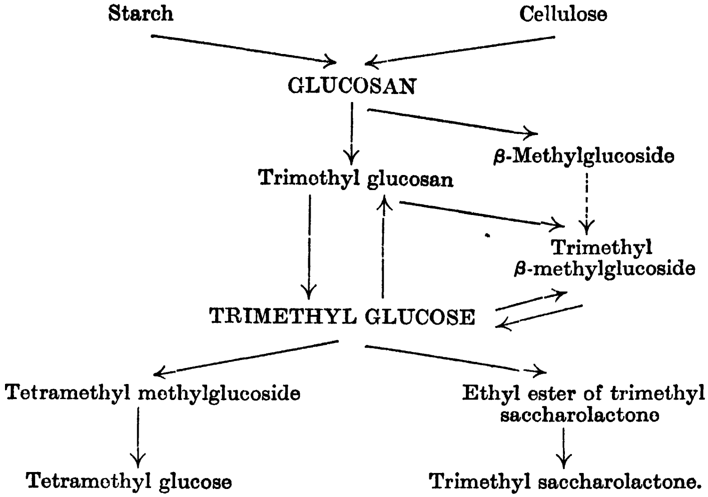


β-Glucosan.

The above formulæ are based on Böeseken's structure for α- and β-glucose, and lead at once to the conclusion that lævo-glucosan is derived from β-glucose. This agrees with the formula put forward by Pictet (*Helv. Chim. Acta*, 1920, **5**, 649) and the β-configuration was confirmed in the following way. β-Glucosan was heated at 100° with methyl alcohol containing 0·5 per cent. of hydrogen chloride, the time of treatment being varied so as to arrest the reaction before the methylglucoside first formed had assumed equilibrium with its stereoisomeride. The crystalline product invariably contained a greater proportion of the β-isomeride than was found in the equilibrium mixture by Jungius (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, **6**, 99), thus indicating that β-methylglucoside is the first product when the glucosan ring is opened.

Parallel experiments conducted on trimethyl glucosan gave a similar result, and the reaction yielded mainly the crystalline trimethyl β-methylglucoside, m. p. 86—88°. As this particular glucoside had not been previously obtained in the β-form, the compound was prepared directly from trimethyl glucose. The two preparations proved to be identical in every respect, thus confirming the β-configuration of lævo-glucosan.

It is now possible to trace the main reactions which are responsible for the formation of β-glucosan from cellulose. In the course of the dry distillation, acids are produced in considerable quantity with the consequent formation of glucose. The β-form of the sugar then undergoes dehydration and distils forward as the anhydride. It may be remarked that the distillation under diminished pressure of carbohydrates and their derivatives is greatly affected by the speed of heating. When the time of contact with the hot surface is reduced to a minimum it is possible to remove the volatilised material before appreciable decomposition takes place. Thus, we find that, under conditions described in the experimental part, not only β-glucosan but both α- and β-methylglucosides may be distilled unchanged in practically quantitative amount. These examples show that many factors are operative in determining when a carbohydrate or its derivatives may be found in the products of dry distillation, but it is evident that any compound which yields β-glucose on hydrolysis may be expected to yield β-glucosan in Pictet's reaction. The complete series of reactions carried out in the course of the research is shown in the following scheme :


Starch
Cellulose
GLUCOSAN
β-Methylglucoside
Trimethyl glucosan
Trimethyl β-methylglucoside
TRIMETHYL GLUCOSE
Tetramethyl methylglucoside
Ethyl ester of trimethyl saccharolactone
Tetramethyl glucose
Trimethyl saccharolactone.

Discussion of Results.

The essential point which has emerged as an issue of the present research is that β-glucosan bears no structural relationship to cellulose. Pictet's views appear to have been widely accepted, but have not escaped criticism, and, in particular, it has been pointed out that they are inconsistent with the fact that cellulose can be degraded to cellobiose, and starch to maltose. It has now been established that the conversion of cellulose into β-glucosan is essentially a dry distillation of β-glucose. Our results thus support the opinion expressed by Hess and Mittelsbach (*Zeitsch. Elektrochem.*, 1921, **26**, 232) and no other conclusion can be drawn than that the production of glucosan from cellulose is adventitious.

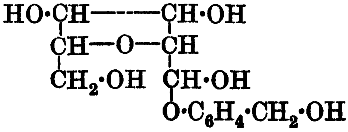
Recently, however, Reilly (*Helv. Chim. Acta*, 1921, **4**, 616) has replied to Hess and produced evidence which he claims to substantiate Pictet's polymerisation theory. Reilly subjected methylated celluloses to dry distillation under diminished pressure and obtained a " dimethyl lævo-glucosan " from which a " dimethyl glucose " was obtained. These results have no bearing on the problem at issue. An incompletely methylated cellulose, irrespective of its constitution, would give products of the above composition, and the conversion of the dimethyl glucose into a trimethyl glucose which could be compared with Denham and Woodhouse's product would be valueless (even if it were possible), as there is no means of determining which of the hydroxyl positions available for methylation should be substituted. The results we now contribute supply the necessary information and lead to an entirely different conclusion.

With regard to the structure of β-glucosan, the formula we suggest agrees with that which Pictet finally supported (*Helv. Chim. Acta*, 1920, **3**, 649), but it must be pointed out that his explanation of the isomerism displayed by the so-called "*d*-" and "*l*-" glucosans is most improbable. He regards both anhydrides as derived from the same form of glucose, the anhydride ring being an ethylene oxide for the *d*-form, and a hexylene oxide for the *l*-isomeride. In all probability *d*-glucosan will be found to be an anhydride of α-glucose just as *l*-glucosan is now shown to be the 1 : 6-anhydride of β-glucose.

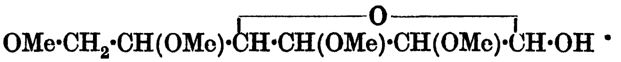
Suggested Relationship of β-Glucosan to Natural Glucosides.

In developing the idea that β-glucosan is a constituent part of important carbohydrates, Pictet (*Helv. Chim. Acta*, 1919, **2**, 698) has proposed radical alterations in the constitution of certain natural glucosides. Recognising that many of these compounds share with β-glucosan the property of being lævorotatory, he suggests that they are structurally related. So many objections may be offered to this opinion that it is needless to summarise them. The fact that typical glucosides, such as salicin, give β-glucosan on dry distillation is regarded by Pictet as confirmatory evidence, but if reference to the standard literature on the sugars is made it is inconceivable that such views will find acceptance. Natural glucosides are lævorotatory in that essentially they are derivatives of β-glucose, and it may be recalled that when Nef put forward the idea that α- and β-glucosides differed structurally, and not in the stereochemical position of the glucosidic group, his arguments were convincingly refuted by Fischer.

One of the test cases quoted by Pictet may now be criticised in detail in order to show how divergent his glucoside formula is from well-established reactions. He suggests for salicin the structure



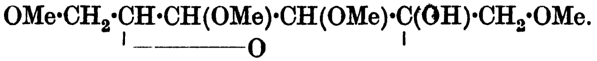
Quite apart from the fact that a substance of the above type would probably be a reducing sugar and not a glucoside, it is evident that no attention has been directed to the constitutional study of salicin undertaken by Irvine and Rose (T., 1906, **89**, 814). These workers prepared, both synthetically and directly from salicin, a well-defined, crystalline pentamethyl salicin. This, in turn, gave on hydrolysis tetramethyl glucose of the butylene-oxide type :



$$\mathrm{OMe{\cdot}CH_2{\cdot}CH(OMe){\cdot}\overbrace{CH{\cdot}CH(OMe){\cdot}CH(OMe){\cdot}CH}^{O}{\cdot}OH}$$

In other words, salicin is constituted on the same model as β-methylglucoside, so far as the sugar chain is concerned.

On the other hand, according to Pictet's formula the only alkylated sugar obtainable from pentamethyl salicin would be a tetramethyl hexose of the structure shown below :



$$\mathrm{OMe{\cdot}CH_2{\cdot}\underbrace{CH{\cdot}CH(OMe){\cdot}CH(OMe){\cdot}C}_{O}(OH){\cdot}CH_2{\cdot}OMe.}$$

The above sugar has already been described and is not a derivative of glucose, but is the tetramethyl fructose of the butylene-oxide type (Steele, T., 1918, **113**, 257). It bears no relationship to tetramethyl glucose, which, as stated, has long been known to result when pentamethyl salicin is hydrolysed.

The acceptance of Pictet's views would thus mean that the naturally-occurring glucosides showing a lævorotation are not glucosides but fructosides. It may be remarked that, since putting forward his glucoside formula, Pictet has revised his opinion as to the constitution of glucosan. He has not, however, corrected his formulæ for salicin and other natural glucosides, nor would it be possible to do so without assuming rupture of the butylene oxide ring. This again would preclude the possibility of pentamethyl salicin yielding tetramethyl glucose or of being synthesised from this sugar.

These criticisms are offered in the hope that the permanent literature of the sugars will not be further complicated by speculations on structure which are based on insecure evidence and are made without reference to previous work.

EXPERIMENTAL.

Preparation of β-Glucosan.

The conditions laid down by Pictet and Sarasin were followed and in the first instance a specially pure form of fibrous cellulose was employed. From the semi-crystalline distillate pure β-glucosan was isolated, and similar results were obtained with cotton wool and filter paper. The use of cellulose in any form is inconvenient. The low thermal conductivity of the material prevents uniform heating of the mass and although in small-scale working the yield of distillate quoted by Pictet (44 per cent. of the cellulose taken) was verified, it was seriously diminished when larger quantities were employed. The bulk of the glucosan required was therefore prepared from starch, used in the form of lumps as the powdered material proved unsuitable owing to the fine particles being carried forward mechanically during the vacuum distillation.

The distillation apparatus was made of quartz and was attached to an efficient condensing system, the vacuum being provided by a Geryk oil pump driven electrically at a speed which kept the pressure at 8—10 mm. In the earlier experiments, heating was effected by immersion in a bath of fusible metal, but in large-scale working superior yields were obtained by heating with the free flame. This must be conducted cautiously at first, as otherwise the starch swells and fills the side tube of the flask, but in the later stages of the distillation both the bottom and sides of the flask were heated with powerful burners so as to prevent refluxing.

In each experiment 100 grams of starch were used, giving from 43—48 grams of a dark, viscous syrup which distilled at 250—300°/10 mm., a carbonaceous residue remaining behind. The syrup, on keeping in shallow vessels, gradually crystallised, and after draining on a porous plate the material was washed with cold acetone and crystallised from boiling alcohol. Thereafter, the product was decolorised by boiling in aqueous solution with animal charcoal and, on recrystallisation from water, gave pure β-glucosan. In all, 4300 grams of starch yielded 1670 grams of syrup, from which 230 grams of pure glucosan were isolated. The yield is thus less than 6 per cent. of the polysaccharide used, but may be much improved by modifications which will be described in another communication.

Preparation of Trimethyl β-Glucosan.

This reaction was carried out on several occasions, but only one typical experiment need be quoted. Twenty-five grams (1 mol.) of glucosan were dissolved in 132 grams (6 mols.) of methyl iodide mixed with 115 c.c. of methyl alcohol. Methylation was effected by the gradual addition of 108 grams (3 mols.) of silver oxide and the reaction was continued at the boiling point of the liquid for seven hours. On isolating the product in the usual manner, a viscous syrup remained which, as a rule, was fully soluble in methyl iodide. Complete methylation resulted when a second treatment with the above proportions of the methylating reagents was given, very little, if any, extraneous solvent being employed. The product was extracted with boiling ether and the filtered extract dried and evaporated. In this way 27 grams of a mobile syrup remained which boiled indefinitely at 140—170°/20 mm. On repeated fractionation, the material was separated into two components, the main fraction boiling at 145—150°/18 mm. and the less volatile liquid at 165—169°/17 mm. The distillate of lower boiling point crystallised readily, and the solid was removed by suction and recrystallised from ether. The product separated in aggregates of rhombohedra, and an average specimen melted at 62°, the maximum recorded being 66°. The boiling point of the purified material was 135·5°/12 mm. (Found: C = 52·76; H = 7·75; OMe = 45·5. $C_9H_{16}O_5$ requires C = 52·94; H = 7·84; OMe = 45·6 per cent.). The molecular weight, determined in benzene by the ebullioscopic method, was 212 ($C_9H_{16}O_5$ requires M = 204), so that the compound was monomolecular.

Solvent.	*c.*	$[\alpha]_D^{20°}$.
Acetone	5·0000	− 63·6°
Water	5·0000	− 63·5
Methyl alcohol	4·9916	− 53·2
Benzene	5·0000	− 48·5

Conversion of Trimethyl β-Glucosan into Trimethyl Glucose.

A 7·5 per cent. solution of trimethyl glucosan was prepared in water containing 3·6 per cent. of hydrochloric acid and the solution was heated on a boiling-water bath, polarimetric readings being taken at intervals of an hour. The rotation gradually altered from lævo to dextro, and finally, after six to eight hours, attained a permanent value which varied between + 70·0° and 76·6°. Thereafter the acid was neutralised with lead or barium carbonate, and the solution filtered and evaporated to dryness in a vacuum. On extracting the residue with acetone and removing the solvent, a syrup remained. This was essentially trimethyl glucose contaminated with traces of lead compounds which were, however, left undissolved on extraction with ether. The purified sugar was distilled (b. p. 160—164°/0·2 mm.) and rectified in the course of a second distillation. The refractive index, n_D, was 1·4780 (Found: C = 48·58; H = 8·09; OMe = 41·9; M, in boiling benzene solution, = 231. $C_9H_{18}O_6$ requires C = 48·64; H = 8·10; OMe = 41·9 per cent.; M = 222).

The sugar was a colourless viscid syrup which showed no tendency to solidify when nucleated with the crystalline trimethyl glucose prepared from cellulose. It failed to form an osazone and yielded a crystalline anilide only with difficulty, but gave a well-defined crystalline glucoside when condensed with methyl alcohol.

The following observations were made on the optical activity of the sugar:

Solvent.	*c.*	$[\alpha]_D^{20^\circ}$ varied from
Water	4·086	$+ 42·7^\circ$ to 66·8
,, ...	2·276	$+ 47·3$ —
Acetone	3·400	$+ 60·8$ to 70·5
Methyl alcohol	3·366	$+ 55·6$ to 69·1

As explained in the introduction, different preparations of this sugar give widely divergent specific rotations, and the values quoted above are the extremes found by us. Repeated distillation depressed the dextrorotation, lowered the hydrogen value, and increased the carbon content, so that the result is evidently due to dehydration and reconversion into trimethyl glucosan.

This was confirmed by heating a specimen showing the specific rotation $+ 45·9^\circ$ with 6 per cent. hydrochloric acid. The dextrorotation then increased rapidly and on again isolating the sugar it gave $[\alpha]_D + 62·2^\circ$ in aqueous solution.

Constitution of the Trimethyl Glucose obtained from Trimethyl Glucosan.

Conversion into Tetramethyl Glucose.

Two methylations by means of the silver oxide reaction gave tetramethyl methylglucoside ($n_D = 1·4469$). This was hydrolysed in the usual manner and as the preparation was a mixture of α- and β-isomerides the rotation showed the customary rise and fall in the dextro-sense. The tetramethyl glucose thus produced melted at 96°, gave satisfactory analytical figures, and showed mutarotation in absolute alcohol ($[\alpha]_D + 99·4^\circ \longrightarrow 84·3^\circ$). In water, the optical change was $[\alpha]_D + 92·2^\circ \longrightarrow 83·8^\circ$, and these values agree well with the standards for tetramethyl glucose.

Oxidation of Trimethyl Glucose.

In order to decide which of the two possible trimethyl glucoses was present the sugar was oxidised in the usual manner with nitric acid (D 1·2). A variation was, however, introduced in that after the removal of the bulk of the nitric acid by successive concentration to half bulk at 40°/20 mm., alcohol was added and the evaporation repeated. This treatment was continued and the product was finally heated in absolute alcohol containing a trace of hydrogen chloride. In this way the sugar was converted into the ethyl ester of trimethyl saccharolactone, which was purified by distillation under 0·4 mm. pressure (Found: C = 50·33; H = 6·78; OMe = 35·2; OEt = 17·03. $C_{11}H_{18}O_7$ requires C = 50·38; H = 6·87; OMe = 35·5; OEt = 17·2 per cent.). The compound was a pale yellow, mobile liquid and contained one lactonic and one esteric group (0·2005 gram required 12·55 c.c. of *N*/10-alkali in place of the calculated amount, 12·75 c.c.). Moreover, when dissolved in aqueous alcohol, the compound showed the decrease in dextrorotation characteristic of lactones in this series.

Solvent.	*c.*	$[\alpha]_D^{20^\circ}$.
Absolute alcohol	1·016	+ 73·4°
50% Aqueous alcohol	1·106	+ 65·8° → 41·6° in seventy hours.

The ester was thereafter converted into the corresponding acid by heating in aqueous alcoholic solution with excess of barium hydroxide. After one hour at 100°, the excess of alkali was precipitated with carbon dioxide and the filtered liquid evaporated at 50°/20 mm. The barium salt thus obtained was decomposed with sulphuric acid and the lactonic acid isolated in the usual manner (Found: C = 46·02; H = 6·24; OMe = 38·9. $C_9H_{14}O_7$ requires C = 46·15; H = 5·98; OMe = 39·7 per cent.). The presence of one carboxyl and one lactonic group was confirmed by titration, and the change in specific rotation in 50 per cent. aqueous alcohol was + 76·1° → 54·8°. These constants are in good agreement with those previously determined for trimethyl saccharolactone.

Conversion of β-Glucosan into β-Methylglucoside.

For reasons given in the introduction, β-glucosan was converted into the corresponding methylglucoside under conditions which minimised the interconversion of the α- and β-forms. A 10 per cent. solution of β-glucosan in methyl alcohol containing 0·468 per cent. of hydrogen chloride was heated at 100°, and samples were abstracted at intervals in order to ascertain by methoxyl estimations when the whole of the glucosan had reacted. In this way it was possible to arrest the condensation before the glucosides had attained equilibrium. After forty-one hours' treatment, the crystalline product was isolated and found to consist of a mixture of the isomeric methylglucosides (Found: OMe = 15·2. $C_7H_{14}O_6$ requires OMe = 15·9 per cent.). The amount of pure β-methylglucoside present was 30 per cent., in place of 23 per cent., which is the proportion in equilibrium with the α-form. β-Methylglucoside is therefore the first to be produced when β-glucosan condenses with methyl alcohol, thus proving the β-configuration of the anhydro-compound.

This was confirmed in the course of several experiments. Fo example, the reaction between glucosan and methyl alcohol was arrested when the specific rotation was + 72·3°. The mixed glucosides thereafter isolated consisted of 62·0 per cent. of the α- and 38 per cent. of the β-form. On continuing the condensation the proportion of the α-isomeride increased at the expense of the β-form, and this increase of activity at the end of the reaction confirms that β-methylglucoside is the first product of the condensation.

Conversion of Trimethyl β-Glucosan into Trimethyl β-Methylglucoside.

A 4·4 per cent. solution of trimethyl glucosan in methyl alcohol, containing 0·5 per cent. of hydrogen chloride, was heated at 110°, and samples were withdrawn after the reaction had proceeded for eighty-five hours, one hundred and sixty-six hours, and one hundred and ninety hours respectively. In each case the products were isolated by standard methods and proved to be mixtures of the α- and β-isomeric forms of trimethyl methylglucoside. The β-compound, which crystallised on keeping, was separated by draining on a tile and purified from light petroleum. The compound was deposited in fine needles, m. p. 93—94° (Found: C = 50·78; H = 8·57; OMe = 50·9. $C_{10}H_{20}O_6$ requires C = 50·84; H = 8·47; OMe = 52·5 per cent.). For *c* = 1·5, the specific rotation in methyl alcohol was — 22·9°. When hydrolysed with 2·5 per cent. hydrochloric acid at 100°, the compound was converted into trimethyl glucose, the specific rotation then altering from — 19·6° to + 69·5° (corrected for the hexose formed, + 73·8°).

The liquid form of trimethyl methylglucoside consisted of the α-isomeride retaining some of the β-form in solution. This was shown by the behaviour on hydrolysis with 2·5 per cent. hydrochloric acid. The specific rotation then displayed the characteristic rise and fall significant of the presence of two isomerides of opposite rotation which hydrolyse at different speeds.

Time from start in minutes.	Specific rotation.
0	+69·7°
60	83·6
120	80·0
380	71·3

In this case also, clear evidence was obtained that the reaction of the methylated glucosan with methyl alcohol gave the corresponding β-glucoside in the first instance, as the proportion of the crystalline isomeride steadily diminished with continued heating. Thus, when the condensation was arrested at the end of one hundred and sixty-six hours, the specific rotation of the liquid was + 55·6°. After an additional twenty-four hours' heating, the value had increased to + 104·8° without any alteration in methoxyl content, showing that the final change is the conversion $\beta \longrightarrow \alpha$.

Distillation of β-Glucosan and of α- and β-Methylglucoside.

In view of the opinions expressed in the course of this paper, it was desirable to ascertain the behaviour of β-glucosan when heated under diminished pressure. It was found that when small quantities are used the compound may be distilled unchanged. 2·6 Grams of glucosan were heated in a silica flask connected by a short air-condenser to a receiver which was coupled to a pump. The material was heated with the naked flame. The compound melted and, under a pressure of 9 mm., commenced to sublime, but as the temperature was raised, normal distillation took place and 2·3 grams passed into the condenser and receiver. The product, after recrystallisation from alcohol, was pure β-glucosan, melting at 178—180° and showing $[\alpha]_D$ — 65·4° in aqueous solution.

α-Methylglucoside behaved similarly when heated in small quantities. Thus, 1·4 grams gave 1·3 grams of distillate which solidified to a glass on cooling. On crystallising from alcohol, this material was shown to be pure α-methylglucoside, melting at 167° and giving $[\alpha]_D$ + 155° in water.

β-Methylglucoside gave an equally satisfactory result and the distillate crystallised in the receiver. Without further purification the compound then melted at 104—106°, and this value was unaffected by crystallisation from ethyl alcohol or by admixture with an authentic specimen. The specific rotation in water was — 30·0°, and the distillate thus consisted of pure β-methylglucoside. The above result was not obtained when a metal bath was used as the source of heat, the glucosides then decomposing without distillation.

The authors desire to express their indebtedness to the Department of Scientific and Industrial Research for a grant which enabled one of them to take part in the investigation.

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CXCIX.—*Studies in Emulsions. Part III. Further Investigations on the Reversal of Type by Electrolytes.*

By SHANTI SWARUPA BHATNAGAR.

IN a previous paper of this series (this vol., p. 61), the effects of a large number of electrolytes on the reversal of phases in emulsions prepared with univalent soaps have been described. A complete quantitative investigation on the effects of electrolytes on emulsion equilibrium being of fundamental importance for the elucidation of the mechanism of emulsification, attempts were made to examine whether emulsions prepared with the so-called insoluble emulsifiers of Pickering could undergo a reversal of type under the influence of electrolytes. The effects of volume ratio of the phases and temperature were minimised by carrying out the experiments at about 17—19° and by adding a moderate amount of the emulsifying agent to equal volumes of the two phases. It has been shown that under these conditions (Clayton, "Margarine Manufacture"; Bhatnagar, T., 1920, **117**, 542) the type of emulsion obtained is mainly dependent on the nature of the emulsifying agent. The emulsions were prepared in the manner described in previous papers (*loc. cit.*), and were examined by the drop method of Briggs and confirmed by the electrical method (*loc. cit.*) and under the microscope.

EXPERIMENTAL.

Finely-divided solids like basic salts of copper and nickel were first used by Pickering (T., 1907, **91**, 2002) in preparing concentrated emulsions. No attempts seem to have been made by him or any other investigator in the field to examine whether a reversal of type can be brought about in emulsions prepared in that fashion. Earlier attempts with ordinary, finely-powdered hydroxides of zinc, cadmium, and aluminium brought out nothing new. Later, it was considered desirable to prepare fresh samples of zinc hydroxide for use as emulsifying agent. In order to do so, about 6 grams of pure zinc sulphate were dissolved in about 200 c.c. of water and an excess of potassium hydroxide solution was added, so that all the zinc hydroxide precipitated was dissolved. Small quantities of dilute hydrochloric acid were then slowly added until the precipitate just reappeared. Such a solution, when kept for some time, threw down a moderately large quantity of zinc hydroxide as coagulum. The coagulum and liquid were transferred to a parchment dialyser and left there for five days. The water in the outer vessel was changed from time to time until no more alkali diffused out through the dialyser and the liquid became neutral to litmus. The coagulum was then made up to a litre and transferred to a carefully cleansed, resistance-glass flask. On agitating this suspension with B.P. paraffin or kerosene oil, it was possible to form stable emulsions sensitive to electrolytes, the emulsions prepared by using the alkali-free suspensions of zinc hydroxide forming the water-in-oil type of emulsion, as opposed to those prepared by alkaline zinc hydroxide, which formed the oil-in-water type. The zinc hydroxide coagulum formed by precipitation with ammonia gave similar results in dialysed and undialysed forms as long as the coagulum was kept moist. Dried zinc hydroxide was incapable of forming stable emulsions. Several samples of 20 c.c. of suspension, each of equal weight, were emulsified with 20 c.c. of oil. The quantity of zinc hydroxide in the aqueous phase was approximately 3·2 grams per litre in each case. The effects of various electrolytes were then examined on emulsions prepared by using this suspension alone and with various electrolytes, and some of these results are shown in Table I.

TABLE I.

Zinc Hydroxide.

Amount of aqueous phase = 20 c.c.
Amount of kerosene oil = 20 c.c.
Quantity of zinc hydroxide = 3·2 grams per litre.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl	1	0·0005	W in O	All quite stable.
	2	0·001	„	
	3	0·005	„	
K_2SO_4	1	0·0005	„	
	2	0·001	„	
	3	0·006	„	
$Al_2(SO_4)_3$	1	0·0001	„	
	2	0·001	„	
	3	0·005	„	
K_3PO_4	1	0·001	„	
	2	0·002	–	Separation into layers.
	3	0·003	O in W	
KOH	1	0·001	W in O	
	2	0·0015	O in W	
	3	0·002	„	
NaOH		0·002	„	

In order to obtain further results, coagula of lead oxide, lead carbonate, copper and aluminium hydroxides, casein, lecithin, rosin, and egg-albumin were prepared in a somewhat similar fashion, and some of them are described in detail later on.

Lead Oxide.

Preparation.—By precipitating the insoluble oxide by the action of the hydroxide on a solution of lead nitrate and dialysing the coagulum as in the case of zinc hydroxide.

TABLE II.

Amount of aqueous phase = 15 c.c.
Amount of oil phase = 15 c.c.
Amount of lead oxide = about 4·2 grams per litre.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl	1	0·002	W in O	
	2	0·004	,,	
	3	0·005	,,	Not very stable.
K_2SO_4	1	0·003	,,	
	2	0·0042	,,	
	3	0·006	,,	
$Al_2(SO_4)_3$	1	0·001	,,	
	2	0·003	,,	
	3	0·006	,,	
K_3PO_4	1	0·0021	,,	
	2	0·008	O in W	
	3	0·009	,,	
KOH	1	0·002	W in O	
	2	0·004	O in W	Stable in all other cases;
	3	0·005	,,	

Aluminium Hydroxide.

The aluminium hydroxide was prepared by the action of ammonium hydroxide on a solution of pure aluminium sulphate. The moist precipitate was dialysed in parchment until the internal and the external water was neutral to litmus. This coagulum was made up to a litre and used as described in the case of zinc hydroxide. Some of the results are shown in Table III.

TABLE III.

Amount of aqueous phase = 20 c.c.
Amount of oil phase = 20 c.c.
Amount of aluminium hydroxide = about 3·8 grams per litre.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl	1	0·002	W in O	Not very stable.
	2	0·004		
	3	0·005		
K_2SO_4	1	0·002		
	2	0·003		
	3	0·005		
K_3PO_4	1	0·001		
	2	0·0035		Tendency to separate into two layers.
		0·004	O in W	Stable.
KOH	1	0·001	—	Tendency to separate.
	2	0·0015	O in W	Stable.
	3	0·002		

Casein.

The casein was a pure sample supplied by Messrs. Baird and Tatlock. A weighed quantity was dissolved in $N/10$-potassium hydroxide and gradually precipitated by acetic acid, the coagulum being then dialysed as in previous cases. The results obtained by casein suspensions when the casein was used dry and when precipitated as described were very nearly identical and therefore the results with the former alone are given.

TABLE IV.

Amount of aqueous phase = 20 c.c.
Amount of oil phase = 20 c.c.
Amount of casein per litre of suspension = 1·985 grams.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl		0·005	O in W	Stable.
K_2SO_4		0·005		
$Ba(NO_3)_2$		0·003		
		0·004		
		0·006		
$Al_2(SO_4)_3$		0·001		
		0·003	W in O	Stable, though some water separates on agitation.
		0·004		
K_3PO_4	1	0·003	O in W	Stable.
	2	0·005		
	3	0·006		
$Th(NO_3)_4$	1	0·0001		
	2	0·00035	W in O	Stable, water separating on agitation.
	3	0·0005	,,	
HCl	1	0·0003	O in W	
	2	0·0004	W in O	
	3	0·00045		

Rosin.

The rosin used was the sample known as the "Seven Star Brand." The finely powdered material was shaken for several hours with a large quantity of water to remove any gummy substance which might have been added to it to increase its weight. After being filtered, the powdered rosin was dried in a current of hot air, dissolved in absolute alcohol, and recovered by evaporation of the solvents. The alcoholic solution was slightly acid, which is a well-known property of many of the pure rosins.

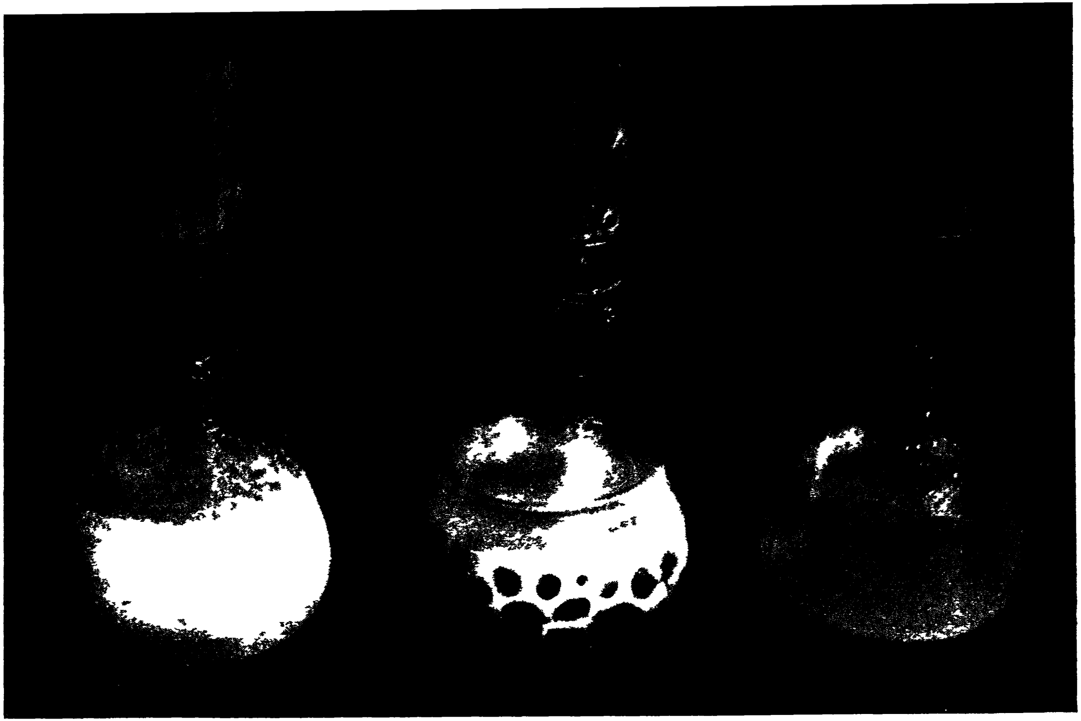
TABLE V.

Amount of aqueous phase = 20 c.c.
Amount of oil phase = 20 c.c.
Amount of rosin = 3 grams per litre.

Electrolyte.		Quantity in gram-mols. per cent.	Type of emulsion.	Stability.
KCl	1	0·002	W in O	Quite stable.
	2	0·003	,,	
	3	0·006	,,	
K_2SO_4	1	0·003	,,	
	2	0·004	,,	
	3	0·006	,,	
K_3PO_4	1	0·003	,,	
	2	0·006	O in W	
	3	0·008	,,	
KOH	1	0·001	W in O	
	2	0·002	O in W	
	3	0·003	,,	

Discussion of Results.

From the results shown in Tables I—VI it is easily seen that aluminium hydroxide, zinc hydroxide, lead oxide, and rosin, prepared according to the methods described above and freed from alkali and alkaline salts like tripotassium phosphate, yield emulsions of the water-in-oil type; casein, lecithin, and egg-albumin yield emulsions of the reverse type. In the case of aluminium hydroxide, the emulsions are unstable in the region water-in-oil. The addition of a small quantity of potassium hydroxide, tripotassium phosphate, or sodium carbonate to the aqueous phase makes emulsions of the oil-in-water type quite stable, and the original, unstable water-in-oil type of emulsion can be reproduced by the addition of a small amount of an acid. Just before the point of complete inversion there is a tendency for the emulsions to go through a zone of instability, and in most cases, especially when the quantity of the emulsifying agent is large, this zone of



Stable oil in water emulsion

Unstable emulsion.

Stable water n oil emulsion

[To face p 1765, Trans

instability can be seen. Plate I, which represents the oil-in-water type, the unstable zone, and the water-in-oil type, is a photograph of emulsions prepared by using lead oxide as emulsifying agent, the reversing electrolyte employed being potassium hydroxide.

It is interesting to note that all emulsions described in this paper can be made to undergo a reversal of type by suitable electrolytes, and the following empirical rules appear to hold good:

1. An emulsion of water in oil can be transformed into one of oil in water by electrolytes having reactive anions like OH' and PO_4'''.
2. An emulsion of oil in water can be transformed into the reverse type by electrolytes having reactive cations like $H^{\cdot}$, $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and $Th^{\cdot\cdot\cdot\cdot}$.

A somewhat similar conclusion has been drawn by Clowes (*J. Physical Chem.*, 1916, **20**, 407), who showed an intimate connexion between the effect of electrolytes on the permeability of soap films to water and the reversal of phases in emulsions. Employing a modification of Donnan's pipette, he obtained some interesting results, which showed that the protective ratios of various electrolytes on soap films are approximately logarithmic and correspond roughly with the precipitating effects exerted by the cations in question on soap dispersed in water. The fact that similar, approximately logarithmic, ratios have been observed during the study of the effects of bi- and ter-valent cations on a variety of colloidal and biological systems (Loeb and Beutner, *ibid.*, 1913, **17**, 288) lends strong support to the view that we are dealing with adsorption phenomena. In the light of these results, Clowes made the significant classification of these antagonistic electrolytes into two groups. "The first consists of di- and tri-valent cations, etc., which possess a more readily adsorbed kation and promote the formation of the emulsion of water-in-oil; the second consists of alkalis, salts of monovalent kations and of di- and tri-valent anions which possess a more reactive and more readily adsorbed anion, and appear to exert the reverse effect of promoting the formation of oil dispersed in water."

According to Bancroft, the type of emulsion obtained depends on whether the emulsifying agent is more soluble in water or in oil. The introduction of the idea of solubility in one phase or the other is an extension of the rule, first put forward by Pickering, that the main factor determining the formation of one type or the other is whether the emulsifying agent is more easily wetted by the oil or by the water. The original view of Pickering is to be preferred; first, because the physical explanation of the phenomenon as given by Bancroft introduces certain complications into our ideas of interfacial tension, and it is by no means easy to understand the two interfacial tensions of a film formed by the concentration of the dissolved substance at the interface according to the Gibbs-Thomson law, and more especially so when the film is assumed to be freely permeable to at least one of the two phases of the emulsions; secondly, for the reason that some bivalent soaps like calcium oleate, barium linoleate, calcium linoleate and palmitate, barium oleate, and zinc stearate, etc., are almost as insoluble in kerosene oil and benzene as in water, and certain univalent soaps, like sodium and potassium oleates, stearates, and linoleates, are soluble in oils as well as in water. Further, there are many substances which dissolve either in water or in oil and lower the surface tension and yet do not form emulsions. Donnan and Terroine, Mayer, Schaeffer (*Compt. rend.*, 1908, **146**, 484), and lately Fischer, Hooker, and Clayton (*J. Soc. Chem. Ind.*, 1919, **38**, 113T—118T) have pointed out that the emulsifying agent must be colloidal in nature, and it is probable that an explanation of the reversal of type by electrolytes is to be found in the nature of the adsorption by the colloidal surface films which envelop the globules. It is no doubt true that one may get some idea of the wetting power of a liquid by its property of dissolving a particular substance, but it is well known that the argument cannot be pushed too far, and many a substance, although insoluble in certain liquids, may yet be wetted by them. It is also well known that soaps are precipitated by the addition of univalent electrolytes, and in fact this action of sodium chloride has been taken advantage of in the technical manufacture of soap in the process of "salting out." It is very difficult to draw a hard and fast line between the effects of univalent electrolytes and of bi- and ter-valent electrolytes on soap solutions, as both of these are adsorption phenomena. On the solubility hypothesis, sodium chloride ought to be capable of changing the type as well as barium chloride. This is, however, contrary to all experience, and the multivalent ions alone are known to cause the reversal of type. There is thus a striking resemblance between these effects of the electrolytes on the reversal of type and the reversal of charge on the colloid emulsifier, and it lends strong support to the view, first put forward by Clowes, that the antagonistic effects of electrolytes are attributable to a balance between the cations on the one hand, and the anions on the other, adsorbed by or reacting with the constituents of the surface film or membrane.

The classical researches of Loeb (*Biochem. Zeitsch.*, 1912, **39**, 127; 1913, **51**, 88) on the effects of reactive cationic electrolytes on lipoids, lecithin, protein, and casein show that they react with them so as to form water-insoluble salts oppositely charged to the original lipoids In explaining the analogous behaviour of certain biological and protoplasmic systems, Mines (*J. Physiol.*, 1912, **43**, 467), Loeb and Beutner (*loc. cit.*), and Clark (*J. Physiol.*, 1913, **47**, 66) have emphasised the importance of both these effects.

The data on the question of the formation of the water-in-oil and the oil-in-water emulsions and their transformation into one form or the other are restricted (1) to results on various soaps by Newman, Clowes, Briggs, and Bhatnagar, and (2) to the work of Pickering and the results embodied in this paper. For the sake of closer comparison, a table of the emulsifying agents so far tried and of the electrolytes which reverse the type is shown below.

TABLE VI.

Emulsifying agent.	Reversing electrolyte: Salts of	Type of emulsion.	Nature of the adsorption compounds; + represents excess of adsorption of positive ions, — represents excess of adsorption of negative ions.
Sodium oleate	Ba, Ca, Sr, Fe, Cr, Al, Cu, Zn, Ni	O in W	+
Carbon	KOH, K_3PO_4	W in O	
Casein	Al, Fe, Th, H	O in W	+
Albumin			+
Zinc hydroxide	KOH, K_3PO_4	W in O	—
Zinc hydroxide (alkaline)	Al, Th, H	O in W	+
Aluminium hydroxide	KOH, K_3PO_4	W in O	
Lead oxide	KOH	,,	
Rosin	K_3PO_4, KOH	,,	
Lecithin	Al, Fe, Th	O in W	+
Univalent soaps	Bivalent and tervalent metals	,,	+

From a close study of the data on the reversal of type in emulsions, it is easily seen that the effects of the electrolytes on the surface film of the globules in emulsions are precisely similar to those on lipoids and protoplasm (Loeb and Osterhout, *loc. cit.*). Substances like tripotassium phosphate and potassium hydroxide have a decided effect on the wetting property of zinc, lead, and aluminium hydroxides, as well as on their surface potential, and a rational theory of emulsification should be capable of including and explaining the facts emphasised here. Wetting power is considered to be connected with interfacial tension, and therefore the two vital factors constituting a complete theory of the reversal of phases will be: (1) the nature of the charge on the emulsifying agent, and (2) its interfacial tension relations with the two phases. Unfortunately, our knowledge of the interfacial tension between solids and liquids is very limited, and for the present the entire data on the reversal of type are in agreement with the empirical rule "*that all emulsifying agents having an excess of negative ions adsorbed on them and wetted by water will yield oil-in-water emulsions, whilst those having an excess of adsorbed positive ions and wetted by oil will give water-in-oil emulsions.*"

It is to be noted that emulsions prepared by gelatin and saponin do not undergo the reversal of type. Cataphoresis experiments on these emulsions show that the addition of bi- and ter-valent electrolytes changes the charge on the oil particles themselves. This is directly opposite to what happens in the case of soaps and casein. In these cases, owing to a complex chemico-adsorption process, the multivalent ions are almost wholly used up by the surface film, and the original negative charge on the oil is not disturbed. The protective film, having adsorbed, say, multivalent cations, is capable of protecting only similarly charged particles, a fact well known in colloidal chemistry. The positive particles in this case are water globules, and it is these particles which are now protected by the adsorbed surface film.

Summary.

1. The effects of various electrolytes on emulsions prepared by the use of zinc hydroxide, aluminium hydroxide, lead oxide, casein, rosin, and egg-albumin as emulsifying agents have been studied.

2. Univalent electrolytes are incapable of reversing the type of soap emulsions, even although they throw out the soap from solution.

3. An excess of adsorbed positive ions on the surface membrane leads to the formation of the water-in-oil type of emulsion. The reverse type is produced by the adsorption of negative ions.

4. All emulsions, whether prepared by soluble emulsifiers such as soaps or by insoluble ones such as zinc hydroxide, follow the empirical rule first suggested by Clowes.

5. Evidence has been accumulated which favours the view that the relative wetting power of the two phases with respect to the emulsifying agent and the surface potential of the membrane between them are the two main factors governing the process of emulsification, and that the reversal of phases in emulsions by electrolytes is brought about by the changes produced in the surface membrane with regard to either or both of these two factors.

The author takes this opportunity of thanking Professor F. G.

Donnan, F.R.S., for his helpful criticism and suggestions. His thanks are also due to Mr. H. I. Higson for taking some photographs of the emulsions and to his friends, Dr. J. C. Ghosh and Mr. J. N. Mukherjee.

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CC.—*Crystallographic Descriptions of some Pyridine and Picoline Derivatives.*

By MARY WINEARLS PORTER.

THE following crystallographic descriptions are an extension of work published in a former paper with T. V. Barker (T., 1920, **117**, 1303) dealing with a study of the morphological and structural effects produced by the mutual replacement of simple organic radicles. The results of the present investigation are summarised in the following table :

No.	Substance.	*a* : *b* : *c*.	β.	Cleavage.
1	$3C_5H_5NMeI,4HgI_2$	0·5106 : 1 : 0·2182	—	{100} and {110}
2	$3C_5H_5NEtI,4HgI_2$	0·6473 : 1 : 0·7728	—	{001}
3	C_5H_5NPrI,HgI_2	1·9897 : 1 : 0·6860	95° 41′	{001}
4	$C_5H_4MeNMeI,HgI_2$	0·8416 : 1 : 1·3697	99° 15′	{010}
5	$C_5H_4MeNEtI,HgI_2$	1·2784 : 1 : 0·5700	93° 6′	{110}
6	$C_5H_4MeNPrI,HgI_2$	1·1654 : 1 : 0·7310	98° 32′	$\{\bar{1}01\}$, {120}, {021}

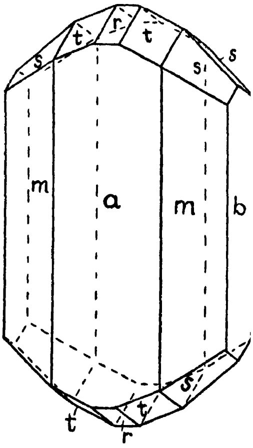
In view of the different type of chemical composition, no crystallographic similarity is to be expected between the first pair of compounds on the one hand and the remaining four on the other. But isomorphism might well be expected within either of the subgroups concerned—especially, perhaps, in the case of the isomeric compounds numbered 3 and 5 in the table. A careful study, however, fails to reveal any close similarity in angles; neither is there any similarity in the cleavage directions. The results, accordingly, afford a strong support to the conclusion drawn in the previous paper, that crystalline form is a highly sensitive, constitutive property, an increment of composition equal to CH_2, or even a slight shift of a simple radicle, being sufficient to cause the molecules to adopt a different type of arrangement when the substance assumes the crystalline state of aggregation.

EXPERIMENTAL.

The methods of preparation and analysis of the various compounds have been fully described previously (*loc. cit.*). The following are the detailed results.

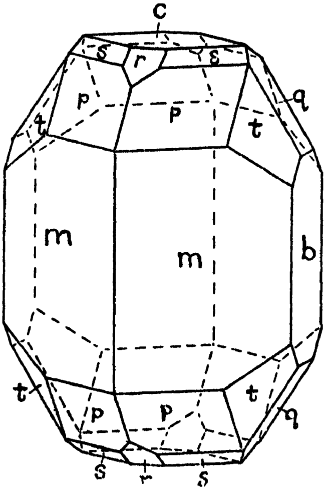
Methylpyridinium Mercuri-iodide, $3C_5H_5NMeI,4HgI_2$.—M. p. 125° (Found: Hg = 32·13. Calc., Hg = 32·27 per cent.). Orthorhombic, $a : b : c = 0{\cdot}5106 : 1 : 0{\cdot}2182$. Forms: *b*{010}, *a*{100}, *m*{110}, *r*{101}, *t*{121}, *s*{141}. The habit is prismatic, as shown in Fig. 1. Six crystals were measured and the results are given below, the deviations of the computed from the measured angular values being added in parentheses.

FIG. 1.



No. 1. *Methylpyridinium mercuri-iodide.*

FIG. 2.



No. 2. *Ethylpyridinium mercuri-iodide.*

	b{010}.	*a*{100}.	*m*{110}.
φ	0° 7′ (−7′)	90° 17′ (−17′)	*62° 57′
ρ	90 0 (0′)	90 1 (−1′)	90 0 (0′)
	r{101}.	*t*{121}.	*s*{141}.
φ	89° 52′ (+8′)	44° 20′ (+4′)	26° 2′ (+3′)
ρ	23 9 (0′)	*31 25	44 14 (−3′)

Cleavages: *a*{100}, good; *m*{110}, imperfect. Optic axial plane, *c*(001); acute negative bisectrix perpendicular to *b*(010); wide axial angle; birefringence and dispersion strong.

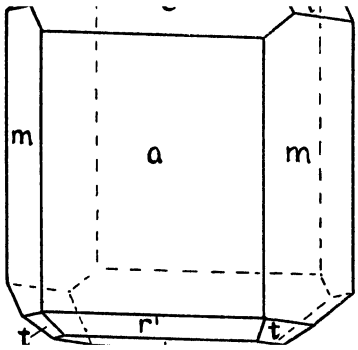
Ethylpyridinium Mercuri-iodide, $3C_5H_5NEtI,4HgI_2$.—M. p. 79° (Found: Hg = 31·44. Calc., Hg = 31·73 per cent.). Orthorhombic, $a:b:c = 0{\cdot}6473:1:0{\cdot}7728$. Forms: *b*{010}, *m*{110}, *c*{001}, *q*{021}, *r*{102}, *p*{111}, *s*{112}, *t*{121}. The habit is prismatic, as shown in Fig. 2. Four crystals were measured with the following results.

	b{010}.	*m*{110}.	*c*{001}.	*q*{021}.
ϕ	0° 0′ (0′)	*57° 5′	—	0° 1′ (−1′)
ρ	90 0 (0′)	90 0 (0′)	0° 0′ (0′)	*57 6

	r{102}.	*p*{111}.	*s*{112}.	*t*{121}.
ϕ	89° 59′ (+1′)	57° 3′ (+2′)	57° 3′ (+2′)	37° 38′ (+2′)
ρ	30 45 (+6′)	54 55 (0′)	35 23 (+3′)	62 50 (+3′)

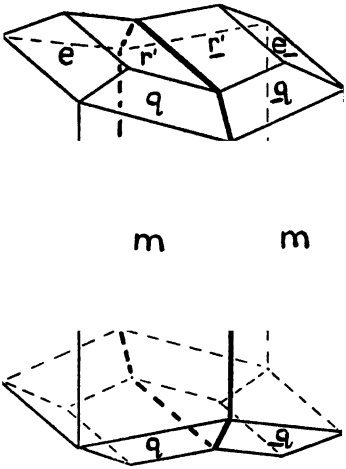
Cleavage: *c*{001}, perfect.

FIG. 3.



No. 3. *Propylpyridinium mercuri-iodide* (*simple crystal*).

FIG. 4.



No. 3. *Propylpyridinium mercuri-iodide* (*twin crystal*).

Propylpyridinium Mercuri-iodide, C_5H_5NPrI,HgI_2.—M. p. 95° (Found: Hg = 28·41. Calc., Hg = 28·45 per cent.). Monoclinic, $a:b:c = 1{\cdot}9897:1:0{\cdot}6860$; $\beta = 95°41'$. Forms: *a*{100}, *m*{110}, *q*{011}, *e*{101}, $r'\{\bar{1}01\}$, $s\{\bar{3}01\}$, $t\{\bar{2}11\}$. The habit, as shown in Fig. 3, is tabular parallel to *a*{100} and elongated along the *c*-axis. Crystals twinned on *a*(100) are frequent (see Fig. 4). Four crystals were measured with the following results.

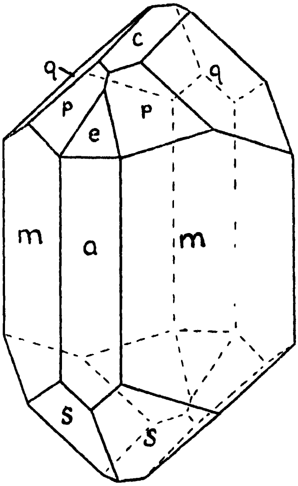
	a{100}.	*m*{110}.	*q*{011}.	*e*{101}.
ϕ	90° 2′ (−2′)	*26° 48′	*8° 15′	90° 9′ (−9′)
ρ	90 0 (0′)	90 0 (0′)	*34 44	23 58 (+3′)

	$r'\{\bar{1}01\}$.	$s\{\bar{3}01\}$.	$t\{\bar{2}11\}$.
ϕ	270° 7′ (−7′)	270° 0′ (0′)	319° 11′ (0′)
ρ	13 53 (−2′)	43 18 (−7′)	42 18 (−6′)

c{001}, fairly good. The optic axial plane is perpendicular to the symmetry plane. The negative acute bisectrix emerges through *c*(001). The double refraction is strong, and the axial angle is wide. Dispersion $\rho < v$.

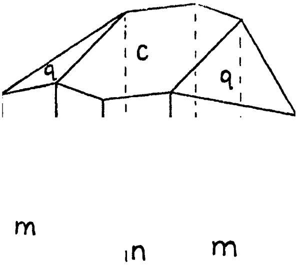
Methyl-α-picolinium Mercuri-iodide, $C_5H_4MeNMeI,HgI_2$.—M. p. 134° (Found: Hg = 29·03. Calc., Hg = 29·03 per cent.). Monoclinic, $a : b : c = 0{\cdot}8416 : 1 : 1{\cdot}3697$; $\beta = 99° 15'$. Forms: *a*{100}, *m*{100}, *c*{001}, *q*{011}, *e*{201}, *p*{111}, *s*{$\bar{2}$11}. The habit is prismatic,

FIG. 5.



No. 4. *Methyl-α-picolinium mercuri-iodide.*

FIG. 6.



No. 5. *Ethyl-α-picolinium mercuri-iodide.*

as shown in Fig. 5. Three crystals were measured, and the results are given in the table below.

	a{100}.	*m*{110}.	*c*{001}.	*q*{011}.
φ	90° 0′ (0′)	*36° 29′	89° 55′ (+5′)	10° 54′ (+3′)
ρ	90 0 (0′)	90 0 (0′)	9 10 (+5′)	40 33 (+3′)

	e{201}.	*p*{111}.	*s*{$\bar{2}$11}.
φ	90° 1′ (−1′)	*43° 1′	307° 53′ (−1′)
ρ	54 40 (−3′)	*49 1	53 56 (−2′)

Cleavage: *b*{010}, imperfect. Optic axial plane *b*(010); the positive acute bisectrix is visible through a section perpendicular to the prism zone. The second mean line α emerges nearly perpendicular to *a*(100). The axial angle is wide.

Ethyl-α-picolinium Mercuri-iodide, $C_5H_4MeNEtI,HgI_2$.—M. p. 99° (Found: Hg = 28·50. Calc., Hg = 28·45 per cent.). Monoclinic,

$a : b : c = 1{\cdot}2784 : 1 : 0{\cdot}5700$; $\beta = 93° 6'$. Forms: *a*{100}, *m*{110}, *n*{210}, *c*{001}, *q*{011}, *s*{201}. The habit is shown in Fig. 6 and is slender prismatic. Five crystals were measured, and the results are given below.

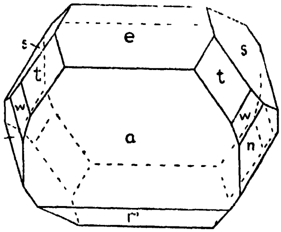
	a{100}.	*m*{110}.	*n*{210}.
	89° 56′ (+4′)	*38° 4′	57° 6′ (+21′)
	90 0 (0′)	90 0 (0′)	90 0 (0′)
	c{001}.	*q*{011}.	*s*{201}.
ϕ	90° 17′ (−17′)	*5° 26′	90° 13′ (−13′)
ρ	3 6 (0′)	*29 48	43 58 (−31′)

Cleavage: *m*{110}, imperfect. Optic axial plane *b*(010). An optic axis is visible through *a*(100) with strong dispersion.

Propyl-α-picolinium Mercuri-iodide, $C_5H_4MeNPrI,HgI_2$.—M. p. 85° (Found: Hg = 27·93. Calc., Hg = 27·89 per cent.). Monoclinic, $a : b : c = 1{\cdot}1654 : 1 : 0{\cdot}7310$; $\beta = 98° 32'$. Forms: *a*{100}, *n*{120}, *s*{021}, *e*{101}, *r*{Ī01}, *t*{221}, *w*{341}. The habit, as shown in Fig. 7, is tabular parallel to *a*(100) and elongated along the *b*-axis. Four crystals were measured and the results are given in the table below.

	a{100}.	*n*{120}.	*s*{021}.
...	89° 58′ (+2′)	*23° 37′	*5° 51′
...	90 0 (0′)	90 0 (0′)	*55 46
	e{101}.	*r*{(Ī01}.	
....	89° 57′ (+3′)	269° 50′ (+10′)	
....	38 11 (−5′)	25 56 (−6′)	
	t{221}.	*w*{341}.	
....	44° 8′ (+1′)	35° 17′ (−14′)	
....	63 47 (+4′)	74 20 (+2′)	

FIG. 7.



No. 6. *Propyl-α-picolinium mercuri-iodide.*

Cleavages: *r*′{Ī01} and *n*{120}, perfect; *s*{021}, imperfect. The optic axial plane is perpendicular to the plane of symmetry and the symmetry axis *b*- is the acute positive bisectrix. Through *n*(120) an optic axis is visible. The dispersion is strong $\rho < v$.

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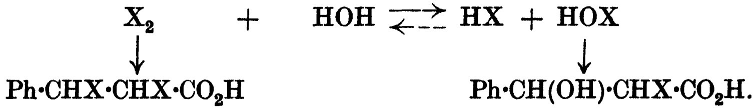
CCI.—*Studies of Halogenohydrins and Related Derivatives in the Cinnamic Acid Series. Part I.*

By JOHN READ and ALBERTA CATHERINE PRITCHARD ANDREWS.

DESPITE the importance of the halogenohydrins of cinnamic acid, the methods hitherto adopted for their preparation are probably little more efficient than those which have been used in making ethylenebromohydrin and other similar derivatives (Read and Hook, T., 1920, **117**, 1214). It is obvious, for example, that the preparation of the bromohydrin of cinnamic acid (α-bromo-β-hydroxy-β-phenylpropionic acid) by boiling the dibromide with water (Glaser, *Annalen*, 1868, **147**, 84; Erlenmeyer, *Ber.*, 1880, **13**, 310) cannot be commended; and although the corresponding chlorohydrin has been made by utilising the principle of direct addition of hypochlorous acid, the yields were unsatisfactory, owing to the conditions adopted. Thus, Glaser (*loc. cit.*, p. 80), in order to avoid the long and troublesome preparation of dilute solutions of hypochlorous acid, passed chlorine into a cold mixture of equivalent proportions of sodium cinnamate and sodium carbonate, thereby obtaining a yield of 35 per cent. of chlorohydrin; and Erlenmeyer and Lipp (*Annalen*, 1883, **219**, 185) described a modified method which was stated to give about 64 per cent. of the calculated amount of chlorohydrin, after allowing for the considerable proportion (22 per cent.) of unchanged cinnamic acid. In contrast to these methods, it has recently been shown that by the action of cold dilute bromine water on an aqueous suspension of cinnamic acid a yield of more than 80 per cent. of bromohydrin is readily obtained (Read and Williams, *J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 558).

It may now be pointed out that since, in the last-named method. the yield of bromohydrin fell to about 50 per cent. when sodium cinnamate was substituted for cinnamic acid, some doubt was thrown upon the advisability of using sodium or potassium cinnamate in the preparation of the corresponding chlorohydrin, according to the methods recommended by the above-mentioned investigators. An examination of the second of these methods, which, judging from its repeated application (compare *Ber.*, 1906, **39**, 788), seems to have been the best hitherto available for the preparation of cinnamic acid chlorohydrin (α-chloro-β-hydroxy-β-phenylpropionic acid), has convinced us that the yield recorded by Erlenmeyer and Lipp is rarely, if ever, attained. Further, there is no justification for Glaser's statement (*loc. cit.*) that hypochlorous acid combines with free cinnamic acid only with difficulty, whilst combination with alkali cinnamates takes place more easily. We have, in fact, been able to devise a simple and expeditious method of effecting almost quantitatively the direct addition of hypochlorous acid to cinnamic acid, by the use of cold chlorine water; it has also been found possible to improve the yield of bromohydrin correspondingly. The reactions concerned may be represented in terms of a mobile equilibrium, in accordance with the scheme already suggested in the similar case of ethylene :



$$\begin{tikzcd}X_2 \arrow[d] & + & HOH \arrow[r, shift left] & HX \arrow[l, shift left, dashed] & + & HOX \arrow[d] \\ Ph\cdot CHX\cdot CHX\cdot CO_2H & & & & & Ph\cdot CH(OH)\cdot CHX\cdot CO_2H.\end{tikzcd}$$

With cinnamic acid and bromine water, the displacement to the right is even more pronounced than with ethylene under similar conditions : at a concentration of 0·08*N* no less than 98 per cent. of the cinnamic acid was transformed to bromohydrin, the corresponding value for ethylene being 94 per cent. In view of the ease with which cinnamic acid reacts with chlorine water or bromine water to produce halogenohydrins, endeavours were made to utilise iodine in a similar way; but up to the present it has not been possible to prepare iodohydrins by this method. Attempts to effect additive reactions with cyanic acid have also failed.

Hitherto, little attention seems to have been directed towards the halogenohydrins of substituted cinnamic acids : in the present paper, some preliminary investigations in this field, dealing with the *o*-methoxycinnamic acids, are described. Like cinnamic acid, these two stereoisomeric derivatives react with bromine water to give almost quantitative yields of bromohydrin, the same crystalline derivative being produced from each. Owing to the simultaneous entry of a bromine atom into the benzene nucleus, it was not possible to prepare the interesting *o*-methoxyphenylacetaldehyde, but the method of Erlenmeyer and Lipp (*loc. cit.*, p. 182), when applied to this new bromohydrin, led easily to 5-bromo-2-methoxyphenylacetaldehyde : it is evident, as a further outcome of this work, that cinnamic acid may similarly be transformed with great facility into phenylacetaldehyde, by the successive action of chlorine water, sodium hydroxide solution, and dilute sulphuric acid.

Although additive reactions of cinnamic acid with chlorine and bromine lead readily to the formation of the two externally compensated, stereoisomeric dichlorides and dibromides demanded by theory (*Ber.*, 1894, **27**, 2039; 1895, **28**, 2235), yet in the similar reactions with hypochlorous and hypobromous acids only one such substance was isolated in each case. Notwithstanding the adoption of conditions which would seem to favour the production of the more labile stereoisomeride, no definite indications of the presence of a more soluble derivative were observed; but it may be mentioned that small quantities of oily material were deposited by the mother-liquors from the recrystallisation of comparatively large amounts of the solid derivatives (compare Erlenmeyer and Moebes, *Ber.*, 1899, **32**, 2377). On the other hand, the crystalline bromohydrin from methylcoumarinic and methylcoumaric acids was associated with pronounced quantities of a viscous oil, which appeared to consist of a slightly impure isomeric derivative and was produced to about the same extent in each case. Like the related dihalogenides and halogenohydrins of cinnamic acid, the new crystalline bromohydrin has been resolved into optically active components, the small molecular rotatory powers of which suggest stereochemical analogy with cinnamic acid derivatives rather than with those of *allo*cinnamic acid (compare Liebermann, *Ber.*, 1894, **27**, 2041). It is interesting to note that although methylcoumarinic acid reacts with chlorine or bromine much more rapidly than does methylcoumaric acid, yet the two acids exhibit no appreciable difference in the ease of their reaction with bromine water. Further, the influence of sunlight, which is marked in the addition of halogens, is negligible in the formation of halogenohydrins from these acids and cinnamic acid.

EXPERIMENTAL.

The Addition of Hypochlorous Acid to Cinnamic Acid.

On passing a slow stream of chlorine, with vigorous stirring, into a suspension of finely crystalline cinnamic acid in about thirty times its weight of ice-cooled water, in accordance with the method used with success in the case of bromine (Read and Williams, *loc. cit.*), a very low yield of chlorohydrin was obtained, and about 60 per cent. of the cinnamic acid was recovered unchanged. This result, which was the same when freshly precipitated cinnamic acid was used, must probably be ascribed to the envelopment of particles of cinnamic acid by the semi-solid aggregations of cinnamic acid dichloride and chlorostyrene which are produced under these conditions. The difficulty was eventually overcome in the following manner:

Cinnamic acid (20 grams) was dissolved in 2*N*-sodium hydroxide solution (67 c.c.) with the aid of an appropriate addition of water (200 c.c.). The resulting solution of sodium cinnamate was then added drop by drop to a large volume (1600 c.c.) of ice-cooled water, acidified with a little (2 c.c.) concentrated sulphuric acid, and a slow stream of chlorine, prepared from hydrochloric acid and bleaching powder, was passed simultaneously into the liquid through a small perforated bulb, admixture being effected by means of vigorous mechanical stirring. Conditions were so adjusted as to maintain a faint yellow tinge in the liquid, and the cinnamic acid liberated from each few drops of sodium cinnamate solution was allowed to react completely before the admission of a further quantity. Reaction occurred rapidly, and when all the cinnamic acid had been introduced the liquid was stirred for some time with passage of air, in order to expel excess of chlorine: the reaction mixture then consisted of a clear colourless liquid, surmounting a small quantity of white solid matter. Preliminary experiments with aqueous solutions of the pure chloro- and bromo-hydrin of cinnamic acid indicated that the amount of chlorine (or bromine) which had reacted to form halogenohydrin and hydrogen chloride (or bromide) could be determined by titrating a small aliquot portion of the liquid with standard silver nitrate solution, using Volhard's method (Read and Hook, *loc. cit.*), a slight correction being applied in accordance with the results of a control experiment in which chlorine was passed into water under similar conditions. Data obtained in this way indicated that more than 95 per cent. of the cinnamic acid had reacted to form chlorohydrin; the corresponding value found for ethylene at the same molecular concentration ($0{\cdot}07N$) was 94 per cent. (*loc. cit.*).

The solid product of the reaction (0·4 gram) consisted of cinnamic acid dichloride, and by extracting the aqueous liquid with light petroleum a small quantity (1·5 grams) of chlorostyrene was isolated. The proportion of cinnamic acid involved in the formation of these by-products is about 9 per cent.; consequently, the yield of chlorohydrin, calculated by difference, is 91 per cent. This result stands in good agreement with the value determined by titration. The ethereal extract of the acid liquid, when dried over sodium sulphate and distilled from the water-bath, yielded a crystalline residue (23·8 grams), which was identified as the anticipated cinnamic acid chlorohydrin, $OH{\cdot}CHPh{\cdot}CHCl{\cdot}CO_2H,H_2O$, m. p. 78—80° (Found: $Cl = 16{\cdot}1$. $C_9H_9O_3Cl,H_2O$ requires $Cl = 16{\cdot}25$ per cent.). The pure substance crystallises well from hot water, as also from hot benzene or toluene; it separates readily from moderately strong aqueous solutions, in the form of a crystalline precipitate, on the addition of dilute sulphuric acid.

The amount of solid chlorohydrin (23·8 grams) actually isolated in the above experiment, when the acid liquid was extracted three times with ether, corresponded with a yield of 80·1 per cent., calculated from the weight of cinnamic acid used. It is essential that the halogen should react with cinnamic acid in presence of the rather large volume of water indicated above: in an experiment conducted with half this volume of water, the other conditions remaining unaltered, about half the cinnamic acid was unaffected, and appreciable quantities of cinnamic acid dichloride and chlorostyrene were produced. It is also advisable to dilute the chlorine with air, in order to minimise the formation of these by-products.

The Addition of Hypobromous Acid to Cinnamic Acid.

The results of the above investigation suggested that the yield of bromohydrin might likewise be increased by precipitating the cinnamic acid, little by little, in the reaction vessel, during the passage through the liquid of a slow stream of air charged with bromine vapour. Upon treating 20 grams of cinnamic acid in this way, reaction occurred with great ease, and a titrimetric determination of the resulting hydrogen bromide indicated that 98 per cent. of the cinnamic acid had reacted to form bromohydrin; the value calculated by difference, taking into account the small amounts of cinnamic acid dibromide and bromostyrene produced, was only slightly lower than this; and the weight (30·3 grams) of solid bromohydrin, $OH{\cdot}CHPh{\cdot}CHBr{\cdot}CO_2H,H_2O$, isolated by extracting the acid liquid three times with ether, corresponded with a yield of 85·4 per cent. After one recrystallisation from hot toluene, the product melted at 120—122° and was anhydrous (Found: $Br = 32{\cdot}5$. $C_9H_9O_3Br$ requires $Br = 32{\cdot}7$ per cent.). By the original method, using finely crystalline cinnamic acid suspended in only three-eighths the above volume of water, the yield of bromohydrin actually isolated was 76·3 per cent. It seems, therefore, that dilution of the solution and dispersion of the cinnamic acid is more important when working with chlorine than with bromine.

In examining various other aspects of this method, it was found that the introduction of the bromine in the form of liquid, rather than as vapour, depressed the yield of bromohydrin from 98 to 82 per cent., a larger amount of cinnamic acid dibromide being formed in this case. At the ordinary temperature, the absorption of bromine was slower than in the cold; more dibromide was formed, and the yield of bromohydrin fell to 89 per cent. Sunlight appeared to have no marked effect on the reaction.

Some Salts of α-Bromo-β-hydroxy-β-phenylpropionic Acid.

During the course of the above work it was noticed that cinnamic acid bromohydrin forms characteristic, well-defined salts, and some of these are now described. The *zinc* salt,

$$(OH\cdot CHPh\cdot CHBr\cdot CO_2)_2Zn,5H_2O,$$

crystallises in lustrous needles when the solution obtained by dissolving zinc carbonate in a warm aqueous solution of the acid is allowed to cool [Found: Br = 24·8. $(C_9H_8O_3Br)_2Zn,5H_2O$ requires Br = 24·8 per cent.]. The *copper* salt,

$$(OH\cdot CHPh\cdot CHBr\cdot CO_2)_2Cu,5H_2O,$$

prepared in a similar manner, forms pale blue needles [Found: Cu = 9·7. $(C_9H_8O_3Br)_2Cu,5H_2O$ requires Cu = 9·9 per cent.].

Special interest attaches to the *brucine* salt,

$$OH\cdot CHPh\cdot CHBr\cdot CO_2H,C_{23}H_{26}O_4N_2,$$

which is highly characteristic of the acid. When equivalent amounts of the acid and brucine were mixed in alcoholic solution, no separation of crystalline material occurred, and evaporation on the water-bath left a vitreous residue. After keeping for a few days, the mass became crystalline when rubbed with methyl alcohol, and by inoculating similar methyl-alcoholic solutions of the mixed acid and base with material obtained in this way the crystalline salt was prepared without difficulty in almost quantitative yield. It was sparingly soluble in water, alcohol, and most of the usual organic solvents, with the exception of chloroform; the solvent best adapted for its recrystallisation and polarimetric examination was 50 per cent. aqueous alcohol. In determining the specific rotatory power of the original separation, a weighed amount was made up to 30·0 c.c. with the solvent at 20° and examined in a 2-dcm. tube: * 0·1867 gram gave $\alpha_D - 0{\cdot}19°$, whence $[\alpha]_D - 15{\cdot}2°$. In the course of several recrystallisations from 50 per cent. aqueous alcohol fluctuations in rotatory power were observed, amounting to a few units on either side of the value recorded above. Small quantities of bromostyrene were produced during the concentration of the solutions. Similar results were observed when brucine was mixed with two molecular proportions of the acid (34 grams) in alcoholic solution: specimens of acid regenerated from various fractions of the salt exhibited only feeble optical activity, the highest value observed being $[\alpha]_D - 4{\cdot}4°$ in 1 per cent. absolute alcoholic solution. From these data it is evident that the two salts, *dAlB* and *lAlB*, produced under the conditions described, give rise to solid solutions, in conformity with the third type of behaviour in such cases distinguished by Pope and Read (T., 1910, **97**, 989). Since well-developed crystals were easily secured, it appeared desirable to record some crystallographic data in this interesting example. We are indebted to Miss Marie Bentivoglio, B.Sc., of the Geology Department, University of Sydney, for the appended description and goniometric measurements, which were made on crystals selected from a fraction having $[\alpha]_D - 13{\cdot}2°$ (Found: N = 4·4. $C_{32}H_{35}O_7N_2Br$ requires N = 4·4 per cent.).

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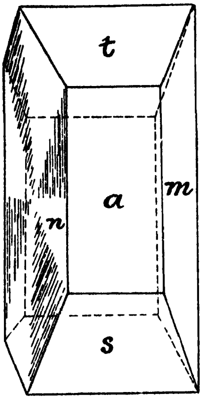
* These conditions were observed in all the polarimetric determinations recorded in this paper.

FIG. 1.



Eight crystals were selected for goniometric work; these were small, rather well-developed, and similar in appearance The crystals are colourless and transparent, and possess highly lustrous faces. The prisms are the dominant form developed; one of these assumes large proportions and is striated to give the general appearance of a star. The pinacoid *a*(100) gives the best reflections obtained from the crystals, and these yielded only fairly satisfactory results. The basal pinacoid and clinopinacoid are entirely absent. Two domes, *s*($\bar{1}$01) and *t*(101), are also represented. No cleavage was observed.

Crystal System: Monoclinic, hemimorphic.

Axial ratios: $a : b : c = 0{\cdot}9095 : 1 : 0{\cdot}9185$. $\beta = 93° 40'$.

The forms developed are: *a*(100), *m*(250), *n*(1$\bar{3}$0), *t*(101), and *s*($\bar{1}$01).

The table of measurements is given below.

	Angle.	No. of measurements.	Limits.	Observed.	Calculated.
am	= 100 : 250	16	66° 46′—67° 40′	67° 06′	67° 06′
$m\bar{m}$	= 250 : 250	8	45 22—45 58	45 48	45 48
an	100 : 130	16	69 39—70 23	69 50	69 50
$n\bar{n}$	= 130 : $\bar{1}$30	8	40 25—41 00	40 40	40 20
at	= 100 : 101	10	42 35—43 10	42 54	42 54
$t\bar{s}$	- 101 : $\bar{1}$01	11	90 24—90 42	90 32	90 32
$\bar{s}\bar{a}$	= 101 : $\bar{1}$00	11	46 20—46 44	46 34	46 34

Observations on the Optical Resolution of dl-α-*Bromo*-β-*hydroxy*-β-*phenylpropionic Acid by means of Cinchonine.*

The description given by Erlenmeyer and Moebes (*Ber.*, 1899, **32**, 2375) of the original resolution of this acid with cinchonine indicates that a single recrystallisation of the first separation of salt (37 per cent.) led to an acid having $[\alpha]_D + 21{\cdot}46°$ in 3 per cent. absolute alcoholic solution, and melting at 119—120°. The value $[\alpha]_D + 22{\cdot}6°$ has also been recorded (*Ber.*, 1906, **39**, 790); and this appreciable discrepancy, taken in conjunction with the above-mentioned behaviour of the brucine salt, suggested a further examination of the cinchonine salt. On repeating the resolution according to the original method, but using six times the quantity of cinchonine salt (132 grams), the first separation, after one recrystallisation from alcohol, yielded a fraction (37·75 grams) having $[\alpha]_D + 12{\cdot}4°$ in 0·75 per cent. alcoholic solution. A second recrystallisation gave material (25·85 grams) having $[\alpha]_D + 11{\cdot}8°$, and the lustrous needles resulting from a third recrystallisation (17·6 grams) had $[\alpha]_D + 12{\cdot}9°$. The acid regenerated from the last-named salt was semi-solid, and after one crystallisation from benzene it gave $[\alpha]_D + 19{\cdot}7°$ in 3 per cent. alcoholic solution. The corresponding values after two successive recrystallisations from benzene were $+ 19{\cdot}6°$ and $+ 20{\cdot}0°$ respectively, and the melting point remained unaltered at 119° (Found : Br = 32·8. $C_9H_9O_3Br$ requires Br = 32·7 per cent.).

The acid regenerated from the mother-liquor of the first separation of cinchonine salt was also somewhat oily, but crystallisation from benzene yielded colourless needles melting at 113—114° and having $[\alpha]_D - 15{\cdot}1°$. Three successive recrystallisations from benzene failed to alter either the melting point or the specific rotatory power of this acid. These results appear to indicate that the two cinchonine salts, *d*A*l*B and *l*A*l*B, have some tendency to form solid solutions, and that it is not possible to purify the partly compensated acids by fractional crystallisation.

The Attempted Addition of Hypoiodous Acid and of Cyanic Acid to Cinnamic Acid.

When cinnamic acid was introduced into an aqueous solution of iodine the colour persisted, and no reaction occurred. A similar result was observed when aqueous solutions of sodium cinnamate and iodine in potassium iodide were admitted separately into a large volume of cold water acidified with sulphuric acid. The process was also varied, without success, by dissolving cinnamic acid and iodine in aqueous sodium hydroxide and adding the mixed solutions to acidified water.

Similarly, mixed aqueous solutions of sodium cinnamate and potassium cyanate were introduced slowly, with stirring, into ice-cooled water acidified with acetic acid, but the formation of an additive product could not be established. Modifications of this process were also tried without success.

These results indicate (1) that iodine water cannot be regarded as a practical source of potential hypoiodous acid, and (2) that cyanic acid has no constitutional similarity with hypochlorous acid or hypobromous acid.

The Addition of Hypobromous Acid to Methylcoumarinic Acid.

Methylcoumarinic acid, when treated with dilute bromine water in the manner outlined above for cinnamic acid, reacted very readily, but it was not possible to isolate any homogeneous product after the passage of one molecular proportion of bromine. Extraction with ether at this stage yielded a viscous oil, from which crystalline material melting indefinitely between 124° and 134° was obtained with difficulty. This gave 10·8 per cent. of bromine by alkaline hydrolysis, whereas the calculated percentage for methylcoumarinic acid bromohydrin is 29·1. The results of combustion analysis ($C = 53{\cdot}0$; $H = 4{\cdot}6$ per cent.) indicated that the product contained unchanged methylcoumarinic acid. Moreover, since 45 per cent. of the bromine used was eliminated as hydrogen bromide, it is evident that nuclear substitution accompanies side-chain addition in this reaction. This interesting conclusion was borne out by the results of further experiments, in which bromine was introduced in the usual manner until the attainment of a permanent faint yellow tinge : a solution of methylcoumarinic acid (20 grams) in 10 per cent. sodium hydroxide (45 c.c.), with the addition of a suitable volume of water (100 c.c.), being added slowly to a large volume (1200 c.c.) of ice-cooled water acidified with sulphuric acid (2 c.c.). The amount of bromine absorbed was slightly more than two molecular proportions; of this, 48 per cent. was eliminated as hydrogen bromide, corresponding with a 96 per cent. yield of a bromohydrin of the type

$$OMe{\cdot}C_6H_3Br{\cdot}CH(OH){\cdot}CHBr{\cdot}CO_2H.$$

It is of interest that the yield of ethylenebromohydrin at a similar concentration ($0{\cdot}08N$) was 93·4 per cent.

Extraction of the above acid liquid with ether gave almost the calculated amount of a viscous, brown oil; this became semi-solid on keeping, and by adding a little light petroleum, followed by sufficient benzene to clear the resulting turbid liquid, it was found possible to collect the crystalline portion by filtration. The yield (33 grams) was 82·9 per cent. of the amount theoretically possible, and the product melted at 145—150°. After two recrystallisations from hot benzene containing a little alcohol, fine, colourless leaflets were obtained, melting at 153—154° and corresponding with the formula given above (Found : $C = 33{\cdot}7$; $H = 2{\cdot}9$; Br, by alkaline hydrolysis $= 22{\cdot}5$. $C_{10}H_{10}O_4Br_2$ requires $C = 33{\cdot}9$; $H = 2{\cdot}8$; $Br/2 = 22{\cdot}6$ per cent.). When dissolved in warm water and oxidised at the water-bath temperature with alkaline potassium permanganate solution, it yielded an acid which, after a preliminary crystallisation from a mixture of ether and light petroleum, separated from a hot aqueous solution in long, slender needles melting at 119°. The properties of this acid corresponded with those of 5-bromo-2-methoxybenzoic acid, described by Peratoner (*Gazzetta*, 1886, **16**, 409) (Found: C = 41·4; H = 3·2. Calc., C = 41·5; H = 3·0 per cent.). Assuming the usual mode of addition of hypobromous acid, the crystalline bromohydrin obtained from methylcoumarinic acid by the above reaction was thus α : *5-dibromo-β-hydroxy-2-methoxy-β-phenylpropionic acid.* It dissolves readily in alcohol or acetone, but only sparingly in chloroform, benzene, or toluene, whilst it is almost insoluble in light petroleum. It is most conveniently crystallised from boiling benzene, with the addition of a little alcohol. When pure, it also crystallises well from hot water, in which it is moderately soluble.

The oily material obtained in the reaction contained a small quantity of the corresponding styrene derivative, but the results of alkaline hydrolysis indicated that it consisted mainly of an isomeride of the above acid (Found: Br = 21·1. $C_{10}H_{10}O_4Br_2$ requires Br/2 = 22·6 per cent.). After keeping for six months, only slight signs of crystallisation were evident, and as yet the substance has not been more fully characterised.

The Addition of Hypobromous Acid to Methylcoumaric Acid.

On introducing methylcoumaric acid into cold bromine water, in the manner already described for methylcoumarinic acid, two molecular proportions of bromine were absorbed before the appearance of a permanent yellow tinge; of this amount, 48·5 per cent. was eliminated as hydrogen bromide, indicating a yield of 97 per cent. of a bromohydrin of the type $OMe\cdot C_6H_3Br\cdot CH(OH)\cdot CHBr\cdot CO_2H$. From the ethereal extract almost the same amounts of crystalline and oily products were obtained as in the case of methylcoumarinic acid. After several recrystallisations from hot benzene containing a little alcohol, the solid derivative melted at 153—154°, and further examination of its properties showed it to be identical with the solid bromohydrin obtained from methylcoumarinic acid (Found: C = 33·7; H = 2·9; Br, by alkaline hydrolysis = 22·4. Calc., C = 33·9; H = 2·8; Br/2 = 22·6 per cent.). The oily product was also similar in appearance and properties to that yielded by methylcoumarinic acid (Found: Br, by alkaline hydrolysis = 19·7 per cent.).

Methylcoumaric and methylcoumarinic acids appeared to react with bromine water with equal ease, and in both cases parallel experiments conducted in diffused daylight and in bright sunlight led to the same results.

The Resolution of dl-α : 5-*Dibromo*-β-*hydroxy*-2-*methoxy*-β-*phenylpropionic Acid into Optically Active Components.*

The *brucine* salt, $OMe\cdot C_6H_3Br\cdot CH(OH)\cdot CHBr\cdot CO_2H,C_{23}H_{26}O_4N_2$, was obtained as a vitreous residue by the evaporation of its alcoholic solution; but crystallisation set in when the amorphous mass was triturated, after a few days' keeping, with methyl alcohol. After this preliminary operation, crystallised brucine (39·5 grams) was added to a hot solution of one molecular proportion of the acid (30 grams) in methylated spirit (150 c.c.). It dissolved immediately, but on removing the solution from the water-bath and seeding it with the crystalline salt, rosettes of fine, colourless needles were slowly deposited (24·5 grams). At a concentration of 1 per cent. in 50 per cent. aqueous alcohol, these gave $[\alpha]_D - 14{\cdot}7°$. By slow recrystallisation from the last-named solvent, the salt was deposited in large, transparent prisms of high lustre. On repeating this process several times, fluctuations in specific rotatory power were noticed, but these were less pronounced than in the case of the brucine salt of cinnamic acid bromohydrin. The lowest numerical value observed was $[\alpha]_D - 12{\cdot}7°$ (Found : N = 3·7. $C_{33}H_{36}O_8N_2Br_2$ requires N = 3·7 per cent.).

The acid obtained from the last-named fraction by treatment with hydrochloric acid and extraction with ether was lævorotatory: 0·7138 gram, dissolved in absolute alcohol as noted above, gave $\alpha_D - 0{\cdot}51°$; whence $[\alpha]_D - 10{\cdot}7°$, and $M[\alpha]_D - 36{\cdot}9°$. The melting point was 148°. When dissolved in hot benzene containing a little alcohol and allowed to crystallise slowly, the acid was deposited in large, transparent prisms, and both the specific rotatory power and the melting point remained unaltered.

Of the two salts, *lAlB* and *dAlB*, the former is thus the less soluble in the example under notice. The two salts appeared to possess a tendency to form solid solutions, and the separation was further complicated by the production of an oily styrene derivative during the concentration of the mother-liquors on the water-bath. The highest numerical value of $[\alpha]_D$ observed for any crystalline separation was $- 23{\cdot}8°$. The impure acid regenerated from the mother-liquor of this fraction was obtained from the ethereal extract as a partly crystalline mass, smelling of the styrene derivative; on washing out the oily impurity with a little benzene, the residual acid melted at 140—142°, and had $[\alpha]_D + 7{\cdot}4°$ in 4 per cent. absolute alcoholic solution. After recrystallisation from benzene containing a little alcohol, the melting point rose to 145° and the value of $[\alpha]_D$ to $+ 8{\cdot}6°$. A second recrystallisation gave a product melting at 148° and having $[\alpha]_D + 10{\cdot}7°$ in 4 per cent. absolute alcoholic solution; whence $M[\alpha]_D + 36{\cdot}9^\circ$. Both melting point and rotatory power were unaltered by further recrystallisation. As the highest values obtained for the dextro-acid are identical with those recorded above for the lævo-acid, and since the two preparations melted very definitely at the same temperature, it seems justifiable to conclude that the two enantiomerides were optically pure. The form assumed by the melting-point curve of their mixtures indicates that the partly compensated acids melt as mixtures of optically active and racemic compounds (Roozeboom, *Zeitsch. physikal. Chem.*, 1899, **28**, 508). The resolution was not facilitated by treating the externally compensated acid with half a molecular proportion of brucine. The cinchonine salt was not obtained crystalline.

5-Bromo-2-methoxyphenylacetaldehyde, $OMe{\cdot}C_6H_3Br{\cdot}CH_2{\cdot}CHO$.

A mixture of α : 5-dibromo-β-hydroxy-2-methoxy-β-phenylpropionic acid (30 grams) and water (150 c.c.) was heated on a boiling water-bath for thirty minutes with a solution of sodium hydroxide (6·8 grams in 20 c.c. of water). On the addition of a 25 per cent. solution of sulphuric acid (25 grams) to the warm liquid, carbon dioxide was evolved and a heavy yellow oil separated. The ethereal extract of this oil, when shaken with a saturated aqueous solution of potassium hydrogen sulphite, yielded a colourless, crystalline bisulphite compound (15·9 grams), which was collected, washed with ether, and decomposed with dilute sulphuric acid. The aldehyde was obtained by extraction with ether in the form of a viscous, pale yellow oil, which showed no tendency to crystallise after keeping for several months. When heated to 200°, it darkened, and at a somewhat higher temperature decomposed. The characteristic *semicarbazone*, $OMe{\cdot}C_6H_3Br{\cdot}CH_2{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, was prepared by adding a warm alcoholic solution of the aldehyde (2 grams in 20 c.c.) to a solution of semicarbazide hydrochloride (2 grams) and sodium acetate (3 grams) in a little hot water. The mixed liquid was well shaken for about twenty minutes and then poured into water. The resulting white precipitate was sparingly soluble in boiling alcohol, from which it crystallised on cooling in rosettes of fine, colourless needles, melting at 185° (Found : N = 14·6. $C_{10}H_{12}O_2N_3Br$ requires N = 14·7 per cent.).

Summary.

1. Halogenohydrins have been prepared in almost quantitative yields by the action, under carefully regulated conditions, of cold dilute chlorine water, or bromine water, on free cinnamic acid.

2. By the interaction, under similar conditions, of methylcoumarinic acid and bromine water, a closely corresponding amount of a mixture of two isomeric bromohydrins of the type

$$OMe\cdot C_6H_3Br\cdot CH(OH)\cdot CHBr\cdot CO_2H$$

has been obtained. The crystalline constituent (m. p. 153—154°), isolated in 82·9 per cent. yield, has been shown to contain a nuclear bromine atom in the *p*-position to the methoxy-group : it has been resolved, with the aid of brucine, into two optically active components having $M[\alpha]_D \pm 36{\cdot}9°$. The optical resolution of cinnamic acid bromohydrin has also been submitted to further examination, with interesting results.

3. No appreciable difference has been observed between methylcoumarinic acid and methylcoumaric acid in their reaction with bromine water.

4. An improved method is indicated for the preparation of phenylacetaldehyde; and 5-bromo-2-methoxyphenylacetaldehyde has been made in a similar way.

5. Attempts to effect the direct addition of hypoiodous acid and of cyanic acid to cinnamic acid have proved unsuccessful.

We express our thanks to Messrs. L. A. Basser, B.Sc., and L. Cash, B.Sc., for preparing the methylcoumaric acid and methylcoumarinic acid used in this work.

Further investigations in this and related fields are in progress.

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CCII.—*The Application of Hofmann's Reaction to Substituted Phthalimides.*

By TOM SIDNEY MOORE, MURIEL TREGARTHEN MARRACK, and ANNIE KATHLEEN PROUD.

THE work described in this paper was carried out to determine whether the application of Hofmann's reaction to substitution derivatives of phthalimide would serve for the preparation in quantity of certain substituted anthranilic acids required for other work; and since in each such reaction two isomeric, substituted anthranilic acids are to be expected, the opportunity was taken of determining the effect of the nature and position of the substituting group on the proportions of the two isomerides produced.

The main results are:

	Total yield per cent.	Proportion of products.
4-Chlorophthalimide	95	3 parts of 4-chloroanthranilic acid; 1 part of 5-chloroanthranilic acid as anhydride.
4-Sulphophthalimide	Trace	Trace of 4-sulphoanthranilic acid; no 5-sulphoanthranilic acid.
3-Acetylaminophthalimide...	55	2 parts of 6-acetylaminoanthranilic acid; 1 part of 2-methylbenziminazole-4-carboxylic acid.

The reaction thus affords a convenient method for the preparation of 4-chloroanthranilic acid, and a possible method for 6-acetylaminoanthranilic acid.

The products obtained by similar treatment of 3- and 4-nitrophthalimides have been already investigated by Seidel and Bittner (*Monatsh.*, 1902, **23**, 418) and by Kahn (*Ber.*, 1902, **35**, 471).

	Total yield per cent.	Proportion of products.
3-Nitrophthalimide	80	All 6-nitroanthranilic acid (Seidel and Bittner). Kahn finds a small quantity of 3-nitroanthranilic acid.
4-Nitrophthalimide	90	4 parts of 4-nitroanthranilic acid; 1 part of 5-nitroanthranilic acid.

Thus in all these cases the derivative in which the amino-group takes up a *meta*-position with respect to the substituting group is produced in the larger quantity, irrespective of the nature of the group and of its position.

The behaviour of 3-acetylaminophthalimide with sodium hydroxide was unexpected. On attempting to estimate the amount of imidic nitrogen present by distilling with excess of alkali and absorption of the ammonia, two experiments gave 2·07 and 2·22 of imidic nitrogen, the theoretical value being 6·86 per cent. The same solution, after standing over-night, gave on distillation more ammonia, and by distilling every day for a week 85 per cent. of the theoretical amount of ammonia was obtained. The correct amount of ammonia was obtained at once if the substance was boiled with hydrochloric acid before the ammonia was distilled off.

Bogert and Jouard (*J. Amer. Chem. Soc.*, 1909, **31**, 483) find that when 3-acetylaminophthalimide is boiled with 5 per cent. potassium hydroxide, the solution on acidification gives 2-methyl-4-quinazolone-5-carboxylic acid, and the formation and the subsequent slow decomposition of this compound in the presence of the strong alkali we used offer a possible, if unlikely, explanation of the slow evolution of ammonia. But examination of the sodium salts isolated from the solution after 20 per cent. of the ammonia had been distilled off, and after 80 per cent. had been distilled off, showed that they were, at any rate mainly, sodium acetylaminophthalamate and sodium acetylaminophthalate respectively. The fact that 3-acetylaminophthalimide undergoes reaction with alkali and sodium hypochlorite at much the same rate as phthalimide itself shows that the slow reaction recorded above cannot be due to slow formation of the salts of the two acetylaminophthalamic acids, since these are intermediate products in the reaction with sodium hypochlorite (Mohr, *J. pr. Chem.*, 1909, [ii], **80**, 1). It thus appears likely that the reaction, which is abnormally slow, is the action of alkali on the salts of the 3- and 6-acetylaminophthalamic acids.

A similar slow reaction with alkali has been recorded by Kolbe (*J. pr. Chem.*, 1884, [ii], **30**, 475) in the case of the closely related compound, anthranilamide.

EXPERIMENTAL.

4-*Chlorophthalic Acid.*—The following method was found to give better yields and to be more convenient than that described by Egerer and Meyer (*Monatsh.*, 1913, **34**, 81). Almost theoretical yields of the acid sodium salt can be obtained by passing chlorine into a solution of 20 grams of phthalic anhydride (or the corresponding amount of the acid) in 200 c.c. of water containing 38·4 grams of sodium hydroxide until crystals are no longer deposited. The pure chlorophthalic acid is best obtained by adding the equivalent amount of dilute sulphuric acid to a solution of the twice-recrystallised acid sodium salt, extracting with ether, and recrystallising the residue after removal of the ether from benzene containing a few drops of glacial acetic acid. Both the acid and its salts retain small quantities of hydrochloric acid and chlorides with great tenacity, and we have never been able to obtain direct from aqueous solution products free from chloride. In any case, it is very difficult to get a specimen of 4-chlorophthalic acid in a condition for analysis. Thus the analysis of a specimen which had been dried in a vacuum for a week indicated that the substance still contained solvent (Found : Cl = 17·03. Calc., Cl = 17·70 per cent.); whilst on heating at 100° continuous loss of weight occurred owing to anhydride formation (Found : after heating for two hours at 100°, Cl = 19·41 per cent.). These observations explain the varying melting points and unsatisfactory analyses recorded by earlier workers (Auerbach, *Jahresber.*, 1880, 862; Alén, *Bull. Soc. chim.*, 1881, [ii], **36**, 434; Claus and Dehne, *Ber.*, 1882, **15**, 321; Krüger, *Ber.*, 1885, **18**, 1759; Egerer and Meyer, *loc. cit.*).

4-*Chlorophthalimide.*—This compound, prepared through the anhydride in the usual way, was allowed to react with sodium hypochlorite under the condition ordinarily used for phthalimide (Eng. Pat. 18246, 1890; *J. Soc. Chem. Ind.*, 1891, **10**, 831). The greater part of the product was precipitated from the alkaline solution left after the reaction on acidification with acetic acid, and a small quantity (about one-tenth of the whole) obtained by addition of copper acetate and subsequent decomposition of the precipitated copper salt with hydrogen sulphide. The total yield was 95 per cent. of the theoretical.

Extraction of the product with light petroleum (b. p. 92—102°) left a residue, m. p. 220°, which, after one recrystallisation from glacial acetic acid, melted at 235—236° and was unaltered by subsequent recrystallisation. This residue formed 80 per cent. of the product obtained by precipitation with acetic acid and 30 per cent. of the product obtained from the copper salt. On distillation with soda-lime, it gave an oil of which the acetyl derivative was identified as *m*-chloroacetanilide. The compound, therefore, is 4-chloroanthranilic acid, for which Cohn (*Monatsh.*, 1901, **22**, 481) also found the m. p. 235—236° (Found: Cl = 20·62. Calc., Cl = 20·70 per cent.).

From the residues left on evaporating the petroleum extracts, an almost white product crystallising in short, white needles, shrinking at 172° and melting at 178—179°, was obtained by fractional crystallisation from benzene and final crystallisation from glacial acetic acid. The substance is soluble in sodium carbonate solution, contains a primary amino-group, and gives *p*-chloroaniline on distillation with lime. The melting point does not agree with either of those given for the expected product, 5-chloroanthranilic acid, namely, 145—148° (Hübner, *Annalen*, 1865, **135**, 111) and 211—212° (Freundler, *Bull. Soc. chim.*, 1907, [iv], **1**, 225). The anhydride, $CO_2H{\cdot}C_6H_3Cl{\cdot}NH{\cdot}CO{\cdot}C_6H_3Cl{\cdot}NH_2$, of 5-chloroanthranilic acid would have the properties of our compound and the same chlorine content (Found: Cl = 22·08. Calc., Cl = 21·85 per cent.), but time and material to establish the identity were wanting.

3-*Acetylaminophthalimide.*—This compound was prepared by the direct acetylation of 3-aminophthalimide, which itself is best obtained by reduction of 3-nitrophthalimide * with stannous chloride in the cold (Bogert and Jouard, *J. Amer. Chem. Soc.*, 1909, **31**, 483).

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* It does not seem to have been recorded that 3-nitrophthalic acid, several specimens of which we examined, crystallises from aqueous solution with two

The behaviour of this substance with sodium hydroxide has already been described (p. 1787). The salt obtained from the alkaline mother-liquor after 20 per cent. of the theoretical quantity of ammonia had been evolved gave, after recrystallisation from water and drying to constant weight, N = 11·25; Na = 9·53. $CO_2Na{\cdot}C_6H_3(CO{\cdot}NH_2){\cdot}NH{\cdot}CO{\cdot}CH_3$ requires N = 11·48; Na = 9·45 per cent. This salt gave ammonia when heated with soda-lime.

From the mother-liquor obtained by heating the imide with sodium hydroxide until 80 per cent. of the ammonia had been evolved, a sodium salt was obtained which gave, after similar treatment, N = 5·10; Na = 17·11. $(CO_2Na)_2C_6H_3{\cdot}NH{\cdot}CO{\cdot}CH_3$ requires N = 5·24; Na = 17·23 per cent.

The conditions used for the reaction of sodium hypochlorite with 3-acetylaminophthalimide were the same as those for 4-chlorophthalimide. From the resulting solution both copper and barium salts may be precipitated, but these are apparently complex compounds, for they are not decomposed by hydrogen sulphide and sulphuric acid respectively. The solution was nearly neutralised with hydrochloric acid, allowed to evaporate to a small bulk, and acidified with concentrated hydrochloric acid. After filtration from a small quantity of tarry matter, the solution was allowed to evaporate to dryness, and the organic matter dissolved out of the residue with absolute alcohol. Fractional crystallisation of the alcoholic solution separated the product into two substances.

The less soluble fraction consisted of small, pale brown crystals easily soluble in methyl or ethyl alcohol, moderately soluble in water, and insoluble in ether, benzene, or chloroform. It remained unmelted at 300°, contained nitrogen, but no amino-group, and was soluble in sodium carbonate solution (Found: N = 15·42. $C_9H_8O_2N_2$ requires N = 15·71 per cent.).

The substance thus appears to be 2-methylbenziminazole-4-carboxylic acid, which might be expected to be formed from 3-acetylaminoanthranilic acid, one of the possible products of the reaction with sodium hypochlorite. On distillation with soda-lime, it gave a product agreeing in all its properties with a specimen of 2-methylbenziminazole obtained by the reduction of *o*-nitroacetanilide.

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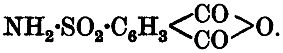
molecules of water, which it loses at 110° (Found: N = 5·65. $C_8H_5O_6N,2H_2O$ requires N = 5·67 per cent.). The anhydrous acid melts at 218°, as does also the hydrated acid when heated slowly. But immersed in a bath at 200°, the hydrated acid melts and re-solidifies (compare Miller, *Annalen*, 1881, **208**, 224; Bogert and Boroschek, *J. Amer. Chem. Soc.*, 1901, **23**, 740).

The second fraction was darker in colour and more soluble in water and the alcohols than the derivative described above, but similarly insoluble in other solvents. It does not melt below 300°, contains a primary amino-group, and is soluble in alkaline solution. On distillation with lime, acetyl-*m*-phenylenediamine was obtained (Found: N = 14·45. $C_9H_{10}O_3N_2$ requires N = 14·43 per cent.). The substance is thus the expected 6-acetylaminoanthranilic acid.

4-*Sulphophthalimide.*—Rée (T., 1886, **49**, 518) prepared the ammonium salt of this compound by heating the diammonium salt of 4-sulphophthalic acid at 190°. We find that on passing dry ammonia into 4-sulphophthalic acid while the temperature is gradually raised to 190°, and maintaining the mass at that temperature until no more ammonia shall be evolved—three to four days—a substance easily soluble in water to give an acid solution and containing the proper percentage of nitrogen for the imide will be obtained (Found: N = 6·16. Calc., N = 6·17 per cent.).

This method of preparation might lead, not only to the desired 4-sulphophthalimide, but also to the isomeric sulphonamide of phthalic anhydride,  $NH_2{\cdot}SO_2{\cdot}C_6H_3{<}\substack{CO\\CO}{>}O$. But from the ease with which ammonia is liberated from the product in alkaline solution we conclude that the substance cannot contain the very stable sulphonamide group, and that it is therefore 4-sulphophthalimide.

The product of the reaction of this substance with sodium hypochlorite was almost entirely the salt of 4-sulphophthalic acid, but by fractional crystallisation a very small quantity of a substance giving the reactions of an aminosulphonic acid, which was soluble in water with a blue fluorescence, was obtained. Since, according to Kalle & Co. (D.R.-P. 138188, 1903), Hollemann (*Rec. trav. chim.*, 1905, **24**, 194) and Kastle (*Amer. Chem. J.*, 1911, **45**, 58), 4-sulphoanthranilic acid and its salts show such a fluorescence in dilute solution, and this acid is one of the possible products, whilst no observation of fluorescence of the other possible product, 5-sulphoanthranilic acid, is recorded in the literature, we conclude that a small amount of the former substance was produced.

Two of the authors (M. T. M. and A. K. P.) desire to record their thanks to the Department of Scientific and Industrial Research for grants made on account of this research.

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CCIII.—m-*Dithiobenzoic Acid.*

By SAMUEL SMILES and JESSIE STEWART.

THE behaviour of *o*-dithiobenzoic acid in sulphuric acid solution has been the subject of previous investigations (T., 1910, **97**, 1290; 1911, **99**, 640; 1912, **101**, 572; 1915, **107**, 1377). Extending this study to other aromatic disulphides, attention was first directed to the *meta*-isomeride. Preliminary experiments with this substance showed that the type of condensation which it undergoes is somewhat different from those observed with the *ortho*-disulphide, and before proceeding further it was necessary to prepare considerable quantities of the acid. The methods at present available for this purpose start either with *m*-aminobenzoic acid, which is converted to the sulphinic acid (Gattermann, *Ber.*, 1899, **32**, 1151), this being finally reduced to the mercaptan, or from *m*-sulphobenzoic acid (Frerichs, *Ber.*, 1874, **7**, 793), from which the dichloride is prepared before reduction of the sulphonic group can be effected. On applying these methods, it was found that for various reasons neither is suitable to the economical preparation of large quantities of the desired material.

A few observers have recorded the production of sulphonyl chlorides by the action of chlorosulphonic acid on aromatic compounds. The cases of benzene- and the toluene-sulphonyl chlorides (*Ber.*, 1909, **42**, 1802, 2057; Harding, this vol., p. 1261) have been thoroughly investigated; other examples are those of *m*-nitrobenzenesulphonyl chloride (D.R.-P. 89997, 1896) and the sulphonyl chloride of *o*-nitrophenol (*Zeitsch. angew. Chem.*, 1920, **33**, 8). These cases, however, appear to be exceptional; in fact, the formation of the sulphonic acid appears usually to have been observed in the action of this reagent. We find, however, on employing suitable conditions, of which the most important is the use of an excess of the reagent, that benzoic acid yields 90—95 per cent. of *m*-chlorosulphonylbenzoic acid. By reduction of this product, *m*-thiolbenzoic acid is readily prepared and thence the required *m*-dithiobenzoic acid is obtained by the usual method of oxidation. Since the sulphonyl chlorides are a very convenient source of most other sulphur derivatives, the investigation of this reaction is being extended to other types of aromatic compound, and it has been found that many of these yield the sulphonyl chloride when treated with chlorosulphonic acid under suitable conditions.

For the product obtained from benzoic acid and chlorosulphonic acid either of two alternative structures (I or II) might be entertained,

$$\underset{\text{(I.)}}{HO{\cdot}OC{\cdot}C_6H_4{\cdot}SO_2Cl} \qquad \underset{\text{(II.)}}{ClOC{\cdot}C_6H_4{\cdot}SO_3H} \qquad \underset{\text{(III.)}}{ClOC{\cdot}C_6H_4{\cdot}SO_2Cl,}$$

but the latter must be rejected, since the substance on reduction yields the corresponding mercaptan. The situation of the carboxyl and sulphonic groups follows from the fact that the chloride (I) and sulphonamide are identical with the corresponding substances prepared from *m*-sulphobenzoic acid. When the liquid dichloride (III) of *m*-sulphobenzoic acid is submitted to hydrolysis by cold water, a solid monochloride is obtained, and it has been considered doubtful whether this product is the sulphonyl or the carboxyl chloride (I or II) (Limpricht and Uslar, *Annalen*, 1858, **106**, 30). The substance is identical with that now obtained directly from benzoic acid with chlorosulphonic acid, and is therefore the chlorosulphonyl derivative (I). Sulphonation of benzoic acid with sulphuric acid under certain conditions yields a small quantity of the *para*-isomeride (Remsen, *Annalen*, 1875, **178**, 278), but this substance has not been detected in the product from chlorosulphonic acid under the conditions adopted.

m-Dithiobenzoic acid in most of its reactions resembles other disulphides, but it is very readily attacked by cold dilute aqueous alkali hydroxide, and this exceptional behaviour has led to a more detailed study of the substance. If the acid be directly titrated with alkali, the value obtained for the equivalent will be normal; but if it be dissolved in excess of cold alkali and the amount of the latter uncombined be then estimated, it will be found that more than two equivalents of alkali hydroxide have been utilised by a molecular proportion of the acid. The reaction which takes place is progressive, and its speed depends on the temperature, the concentration, and on the relative amount of the alkali hydroxide employed. The circumstances are best illustrated by data obtained with solutions at the atmospheric temperature containing six molecular proportions of potassium hydroxide of different concentrations to one proportion of disulphide. The figures quoted represent the number of equivalents of alkali hydroxide which had been employed in reaction with one molecular proportion of the acid after the solution had been kept for the stated periods before titration with hydrochloric acid.

	0 (mins.).	30.	60.	2 (days).	3.	6.
0·1*N*-Potassium hydroxide ...	2·38	2·75	3·0	—	—	4·0
0·2*N*- ,, ,, ...	2·47	3·5	3·7	—	4·0	—
0·5*N*- ,, ,, ...	3·26	3·6	3·75	4·0	—	—
N- ,, ,, ...	3·31	3·65	3·8	—	4·0	—

Examination of the products shows that simultaneous oxidation and reduction take place with rupture of the disulphide system. The chief product is *m*-thiolbenzoic acid; in fact, this substance is readily prepared by acidifying the strongly alkaline solution after it has been kept for a short time. The product or products of oxidation are not so easily recognised, the only one which has been isolated is the disulphoxide, $(-SO\cdot C_6H_4\cdot CO_2H)_2$.

The interaction of alkali hydroxide and aromatic disulphides has previously been noticed in the cases of the diphenyl (Schiller and Otto, *Ber.*, 1876, **9**, 1637; Fromm, *Ber.*, 1908, **41**, 3403) and the di-*p*-nitrophenyl (Fromm, *ibid.*, 1908, **41**, 2267) derivatives. With these substances the reaction was effected by boiling alcoholic solutions of alkali hydroxide, the cold medium having no effect. The products isolated were the corresponding mercaptans and small quantities of the sulphinic acids or their simple derivatives. With the use of the boiling alcoholic reagent, the nature of the reaction is not at all clear, for it is difficult to determine whether or not the formation of mercaptan is due to reduction by this reagent. In the case of *m*-dithiobenzoic acid, where interaction is effected by the cold dilute aqueous reagent, the conditions are simpler.

The formation of the thiol derivative from the disulphide indicates that rupture of the dithio-system has taken place, and since it cannot be supposed that under these conditions the change is due to direct reduction by any reagent present, it must be assumed that the process is primarily one of hydrolysis which is effected by the alkali hydroxide. In fact, no simpler explanation can be given than that represented by the equation

$$HO_2C\cdot C_6H_4\cdot S\cdot S\cdot C_6H_4\cdot CO_2H + H_2O = HO_2C\cdot C_6H_4\cdot SH + HO\cdot S\cdot C_6H_4\cdot CO_2H,$$

in which the mercaptan and sulphenic acid are the primary products. This type of decomposition has been shown to occur with disulphides in sulphuric acid solution, and it has been previously suggested to explain various reactions of substances containing the dithio-group. Attempts to isolate a derivative of the sulphenic acid in the form of an alkyl sulphoxide were not successful, the action of methyl sulphate with the alkaline solution yielding only the *m*-methylthiolbenzoic acid. This result is scarcely surprising in view of the instability of the sulphenic acids and their derivatives. Zincke (*Annalen*, 1912, **391**, 57; 1913, **400**, 1; 1914, **406**, 106) has shown that these substances undergo spontaneous decomposition even in the presence of alkali, yielding disulphides, disulphoxides, and sulphinic acids. Search for the last-named two derivatives showed that the benzoic acid *m*-disulphoxide was formed in small quantity; but the sulphinic acid was not isolated either as such or as the methyl sulphoxide after alkylation of the reacting mixture. It is worth notice that boiling aniline or pyridine attacks the disulphide in the same manner as alkali hydroxide.

It seems impossible to give any definite expression to the reaction beyond the primary hydrolytic change represented in a foregoing paragraph. There is little doubt that the secondary decomposition which appears to give rise to the oxidation products is a complicated process leading to other substances together with the disulphoxide. *m*-Thiolbenzoic acid, which is the chief product of this reaction, may, like other mercaptans, be oxidised to the disulphide. Hence, if there be added to the alkaline reacting mixture some reagent which will reconvert the mercaptan as it is formed to the original disulphide, the latter should be completely converted to the disulphoxide and other subordinate products of the secondary decomposition. Experiments made with iodine confirm this view, good yields of the disulphoxide being obtained.

In this behaviour with cold aqueous alkali, *m*-dithiobenzoic acid is exceptional; other aromatic disulphides which do not contain the acid group appear to be unattacked by the reagent. The patented process (D.R.-P. 193800, 1906) for the preparation of *o*-methylthiolbenzoic acid by heating the dithio-acid with alkali and methyl sulphate appears to indicate that the *ortho*-isomeride behaves like the *meta*-compound. Experiments made under conditions comparable with those described in a former paragraph show that the reaction does take place, but much more slowly. For example, at atmospheric temperature with six equivalents of 0·84*N*-potassium hydroxide to one molecular proportion of *o*-dithiobenzoic acid, after one hour 2·0, after nineteen hours 2·7, and after forty-eight hours 2·95 equivalents of alkali had entered into reaction. The behaviour of other disulphides is being investigated.

EXPERIMENTAL.

m-*Chlorosulphonylbenzoic Acid*, $CO_2H·C_6H_4·SO_2Cl$.

(1) A mixture of benzoic acid and five molecular proportions of chlorosulphonic acid was heated at 125° for one hour in an oil-bath; the evolution of hydrogen chloride had then ceased. The cooled product was poured over crushed ice, and the solid mass ground under ice-cold water, collected, washed with water, and finally dried in a vacuum. The crude sulphonyl chloride melted at about 122°, and after recrystallisation from benzene the pure

material was obtained in colourless prisms melting at 131° (Found: Cl = 16·0; S = 14·3. Calc., Cl = 16·1; S = 14·4 per cent.).

The corresponding sulphonamide was prepared by the action of dilute aqueous ammonia on the chloride. It was recrystallised from a mixture of acetone and water and formed colourless prisms which melted at 233°.

(2) *m*-Chlorosulphonylbenzoyl chloride was prepared from the sodium salt of *m*-sulphobenzoic acid and phosphorus pentachloride (Limpricht and Uslar, *Annalen*, 1857, **102**, 250). The liquid product was mixed with excess of water and set aside. After the lapse of ten days it had become converted to a colourless, crystalline mass. This was collected and recrystallised from benzene; the product melted at 131° and was identical with that obtained from benzoic acid as described in the foregoing paragraph. The corresponding amide was also identical with that prepared from *m*-chlorosulphonylbenzoic acid.

m-*Dithiobenzoic Acid*, $(HO_2C{\cdot}C_6H_4{\cdot}S-)_2$.

Thirty-five grams of zinc dust were added in small quantities from time to time to a solution of 20 grams of *m*-chlorosulphonylbenzoic acid in 150 c.c. of alcohol and 100 c.c. of concentrated hydrochloric acid. The liquid was constantly shaken during the addition, which extended over six hours. Undissolved zinc and a colourless solid (*a*) were collected from the mixture. The clear liquid was mixed with solid ferric chloride, when the required disulphide was precipitated in the crystalline state. This was collected, washed with water and then with acetone before recrystallisation from acetic acid. The product formed cream-coloured aggregates of needles which melted at 246° (Found: C = 54·5; H = 3·6; S = 20·7. Calc., C = 54·9; H = 3·3; S = 20·9 per cent.). Gattermann (*loc. cit.*) gives the melting point of this substance as 242°. *m*-Dithiobenzoic acid is insoluble in water and sparingly soluble in most organic solvents. The solution in sulphuric acid becomes green on agitation with benzene, forming condensation products which are now under investigation. The yield of crude material was about 65—67 per cent. of the theoretical. A further small amount may be obtained from the zinc derivative of *m*-thiolbenzoic acid (*a*) which separates during the reduction. In this process esterification takes place to a certain extent, and a small quantity of ester may be obtained by the addition of water after the removal of the dithiobenzoic acid. The presence of this substance is apt to render purification of the acid difficult, and experiments were made using acetic acid as the solvent in reduction, but the yields, being in the neighbourhood of 35 per cent., were much poorer than that obtained with alcohol as the solvent.

m-*Thiolbenzoic Acid,* $SH\cdot C_6H_4\cdot CO_2H$.

This compound may be prepared by reduction of the disulphide in the usual manner; it is also formed by the interaction of alkali hydroxide with *m*-dithiobenzoic acid. The latter substance was dissolved in excess of aqueous 2*N*-sodium hydroxide. The solution was kept for two hours at 18° and then mixed with excess of dilute sulphuric acid. The copious precipitate was collected and recrystallised from a mixture of alcohol and water, when *m*-thiolbenzoic acid was obtained in needles melting at 146—147°. The substance was converted by ferric chloride to the disulphide, and its properties agreed with those already assigned to the substance.

m-*Methylthiolbenzoic Acid,* $SMe\cdot C_6H_4\cdot CO_2H$.

A solution of 20 grams of *m*-dithiobenzoic acid in excess of *N*-sodium hydroxide was shaken for three hours with two molecular proportions of methyl sulphate. The small quantity of oil which separated during the process was removed by extraction with ether, then the aqueous solution was acidified with dilute sulphuric acid. Ten and a half grams of *m*-methylthiolbenzoic acid were obtained. After recrystallisation from a mixture of alcohol and water, the substance formed feathery needles which melted at 126—127° (Found: C = 56·8; H = 5·0; S = 18·9. $C_8H_8O_2S$ requires C = 57·1; H = 4·76; S = 19·0 per cent.). Thorough search for the sulphoxide or for the sulphone $C_6H_4(CO_2H)\cdot SO_2\cdot CH_3$ which would have indicated the formation of a sulphinic acid during this reaction, was without success.

m-*Methylsulphonebenzoic acid,* $HO_2C\cdot C_6H_4\cdot SO_2\cdot CH_3$, was prepared in the course of this examination by oxidising the methylthiol with permanganate in glacial acetic acid solution. The substance crystallised in shining leaflets on cooling the hot aqueous solution; it melted at 230° (Found: C = 47·7; H = 4·2; S = 16·0. $C_8H_8O_4S$ requires C = 48·0; H = 4·0; S = 16·0 per cent.).

Benzoic Acid m-*Disulphoxide,* $(HO_2C\cdot C_6H_4\cdot SO)_2$.

The preparation of this substance is best effected by the action of iodine on an aqueous alkaline solution of the disulphide. A cold solution of 5 grams of the disulphide in excess of *N*-potassium hydroxide was treated with four atomic proportions of iodine. A solution of the latter in potassium iodide was slowly added from time to time, more alkali being added when necessary to preserve alkalinity of the solution. When all the iodine had been added, the liquid was mixed with excess of dilute sulphuric acid and set aside. After the lapse of a few days, 3·8 grams or a yield of 69 per cent. of benzoic acid *m*-disulphoxide had separated. The substance is readily soluble in hot alcohol, and when recrystallised from this medium it was obtained in small, white needles melting at 220°. The ferric salt, like that of the disulphide, is insoluble in water and soluble in dilute mineral acids. When the solution in sulphuric acid is mixed with a drop of phenetole, a blue colour is slowly developed, hydrolysis to the sulphinic acid then setting in (Hilditch, T., 1911, **99**, 1091) (Found: $C = 49{\cdot}5$; $H = 3{\cdot}1$; $S = 19{\cdot}1$. $C_{14}H_{10}O_6S_2$ requires $C = 49{\cdot}7$; $H = 2{\cdot}98$; $S = 18{\cdot}93$ per cent.). This disulphoxide is also formed by the interaction of the disulphide and cold alkali hydroxide. It may be obtained in small quantity by setting aside the filtrate from the *m*-thiolbenzoic acid described in a foregoing paragraph. The substance then separates in a somewhat impure condition. It was obtained in better yield by boiling the solution of the disulphide in pyridine for one hour. The cold liquid was incompletely neutralised with dilute sulphuric acid, and, after the precipitated disulphide had been removed, the solution was rendered strongly acid. It was then repeatedly extracted with ether, and when this was evaporated the residual oil solidified. The product consisted of the somewhat impure disulphoxide. Similar results were obtained with boiling aniline, but the yields of disulphoxide were even smaller.

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CCIV.—*The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Solutions containing Sucrose.*

By GEORGE JOSEPH BURROWS.

THE influence of sucrose on the rate of hydrolysis of esters by acids has been studied by various investigators. The results obtained by Henri and Larguier des Bancels (*Compt. rend. Soc. Biol.*, 1901, **53**, 784) indicate that sucrose has a slightly accelerative effect on the rate of hydrolysis of methyl acetate. Coppadoro (*Gazzetta*, 1901, **31**, i, 425) concluded that the addition of sucrose had no apparent effect, whilst, more recently, Griffith, Lamble, and Lewis

(T., 1917, **111**, 389) have stated that it diminished the rate of hydrolysis of the ester. The results recorded in the present paper were obtained during an investigation of the influence of various substances on the rate of hydrolysis of esters by acids; they are comparable with those of Griffith, Lamble, and Lewis, nevertheless the author considers that they indicate that sucrose has an accelerative effect.

The subject is of interest in view of the fact that both the ester and the sucrose are being hydrolysed by the acid at the same time.

In all the experiments the temperature was 25°. The solutions in which no sucrose was present were prepared by dissolving the required amount of methyl acetate in water, adding the correct quantity of standard hydrochloric acid, and diluting with water to 100 c.c. (at 25°). In the case of solutions containing sucrose, unless otherwise stated, the latter was added to the solution before diluting to the final volume. The reaction was followed in the usual way by estimating the amount of acetic acid produced by the hydrolysis of the ester after various intervals of time.

The velocity constant k was calculated from the equation :

$$k = \frac{1}{t} \log_{10} \frac{\xi}{\xi - x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ξ is the amount of ester hydrolysed when equilibrium has been attained, and x is the amount hydrolysed in time t (minutes). The values of k were found to be constant for the fraction of the reaction studied.

The equation from which k is calculated is obtained from $\frac{dx}{dt} = k(a - x)$, in which a is the initial concentration of ester. The correct equation for the rate of hydrolysis can be deduced only by considering the reaction as bimolecular and by taking the reverse reaction into account; thus :

$$\frac{dx}{dt} = k_1(b - x)(w - x) - k_2x^2$$

where k_1 is the rate of hydrolysis, k_2 is the rate of esterification, b is the initial concentration of methyl acetate in gram-mols. per 1000 c.c. of solution, w is the initial concentration of water, and x is the number of gram-mols. of ester hydrolysed in t minutes.

From this is deduced by integration (Griffith and Lewis, T., 1916, **109**, 69),

$$k_1 = \frac{1}{tA} \log \frac{A + y + 2(K - 1)x}{A - y - 2(K - 1)x} \cdot \frac{(A - y)}{(A + y)} \quad . \quad . \quad . \quad (2)$$

where $$K = \frac{k_2}{k_1} = \frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acetic acid}} \times C_{\text{alcohol}}} \text{ at equilibrium,}$$

$$y = w + b, \text{ and } A = \sqrt{y^2 + 4(K - 1)wb}.$$

For the solutions considered in this work, K varies only to a small extent. For the purpose of the present investigation, the rate of hydrolysis may be calculated, therefore, from the equation

$$k_c = \frac{1}{tw} \log \frac{\xi}{\xi - x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

so that the values $k_c = k/w$ are considered to represent the rates of hydrolysis of the ester after correcting for the differences in the initial concentrations of water in the various solutions. In this way, the following results (Table I) were obtained for the rates of hydrolysis of 5 per cent. methyl acetate solutions by $N/2$-hydrochloric acid in the presence of various amounts of sucrose.

TABLE I.

Experiment.	Sucrose per cent.	$k \times 10^4$.	w.	$k_c \times 10^6$.
1	0	14·97	52·32	28·6
2	7·5	16·6	49·60	33·5
3	15·0	17·5	46·88	37·3

This increase in the value of k_c may, at first sight, appear to be due to the increase in the concentration of the hydrochloric acid relative to that of the water, resulting from the decrease in the amount of water in the solution. The rate of hydrolysis was therefore determined for a solution containing the same amounts of water, ester, and hydrochloric acid as in the first experiment, to 100 c.c. of which, however, 7·5 grams of sucrose had been added. The mean value of k for this solution was found to be $15·6 \times 10^{-4}$, a value slightly greater than that obtained in experiment 1, although the catalyst had been diluted in the ratio 100 : 105 owing to the increase in the volume produced by the added sucrose. Correcting for this dilution, the value $16·4 \times 10^{-4}$ is obtained. In order to obtain the corresponding value of k_c in this case, it is also necessary to correct for the dilution of the water. Whereas in experiment 1, 52·32 gram-molecules of water were present in 1000 c.c. of the solution, in the other case the same amount was present in 1050 c.c. The value of w is therefore 52·32/1·05, whence $k_c = 32·9 \times 10^{-6}$. This value is considered to be strictly comparable with k_c for a solution containing no sucrose, and it agrees very closely with that obtained in experiment 2, with a solution prepared in such a way that its volume was 100 c.c. This result indicates that the presence of sucrose increases the rate of hydrolysis of methyl acetate by about 17 per cent. for the particular concentrations used.

Similar accelerative effects were observed for the addition of sucrose to other concentrations of acid. These results are collected in Table II. In every case the total volume of the solution was 100 c.c., and it contained originally 5 per cent. of methyl acetate.

TABLE II.

Experiment.	Concentration of acid.	Sucrose per cent.	$k \times 10^4$.	w.	$k_c \times 10^6$.
4	$N/4$	0	7·16	52·35	13·63
5	,,	7·5	8·05	49·83	16·16
6	$N/8$	0	3·50	52·67	6·64
7	,,	7·5	3·99	49·95	7·99

It will be seen that the presence of sucrose increases the rate of hydrolysis of the ester in both the above cases, the effect increasing slightly with decreasing concentration of the acid.

For the hydrolysis of a 2 per cent. methyl acetate solution by $N/10$-trichloroacetic acid at 35°, Griffith, Lamble, and Lewis (*loc. cit.*) obtained the value $k = 1{\cdot}572 \times 10^{-3}$, and for a similar solution to which, however, 8 grams of sucrose had been added, $k = 1{\cdot}602 \times 10^{-3}$, results which compare with those given in the present paper. These authors then determined the rate of hydrolysis in a solution containing the same amounts of acid and water, but an amount of ester equal in volume to the total volume of ester and sucrose used in their previous experiment, and obtained the result $k = 1{\cdot}77 \times 10^{-3}$. They state that this figure is directly comparable with the value $1{\cdot}602 \times 10^{-3}$ obtained for the solution containing sucrose, and conclude that sucrose has a depressing effect.

It is well known that the rate of hydrolysis of an ester is not independent of the initial concentration, but increases with increasing concentration of the ester. This increase has been attributed to the corresponding decrease in the concentration of the water, the latter being considered to have an anti-catalytic effect in such reactions. It is this fact which renders it difficult to study the actual effect of a solute on the rate of hydrolysis of an ester, apart from that due to the change in the concentration of water. When a portion of the water is replaced by sucrose or other substance, one would expect a certain increase in the rate of the reaction resulting from this cause alone. At the same time, the present author considers that Griffith, Lamble, and Lewis have not established their conclusion that sucrose has a depressing effect on the rate of hydrolysis of methyl acetate; at the most, they can only conclude that it has a smaller accelerative effect than the addition of the same volume of methyl acetate to the reaction mixture. Even this, however, has been found not to be the case in the present investigation, in which hydrochloric acid has been used as the catalyst.

The effect of increasing the initial concentration of the ester is shown by the results in Table III, for the rates of hydrolysis of various solutions of methyl acetate by *N*/2-hydrochloric acid.

TABLE III.

Experiment.	Initial concentration of ester per cent.	$k \times 10^4$.	w.	$k_c \times 10^6$.
8	2·5	14·81	53·72	27·6
9	5·0	14·97	52·32	28·6
10	10·0	15·94	49·60	32·1

The value of k_c for a solution containing initially 5 c.c. of ester and 5 c.c. of sucrose ($k_c = 33{\cdot}5 \times 10^{-6}$) is greater than that for a solution containing 10 c.c. of methyl acetate. These results indicate that the rate of hydrolysis of the ester is increased to a greater extent by adding sucrose than by adding a further quantity of ester equal in volume to that of the sucrose.

Finally, the conclusion that sucrose has a definite accelerative effect is further supported by comparing the results given above with that obtained for a solution in which part of the water is replaced by an indifferent substance such as acetone. The rate of hydrolysis of 5 per cent. methyl acetate by *N*/2-hydrochloric acid in aqueous acetone solution containing 20 per cent. of acetone by volume was found to be $14{\cdot}03 \times 10^{-4}$. In this case $w = 42{\cdot}46$, whence $k_c = 33{\cdot}0 \times 10^{-6}$. The corresponding value of k_c for a solution containing 5 per cent. of acetone by volume is $29{\cdot}1 \times 10^{-6}$, which is smaller than the value for a solution containing 5 per cent. of sucrose by volume. It follows that the increase observed for a solution containing sucrose cannot be attributed entirely to a decrease in the total amount of water in the solution.

THE UNIVERSITY OF SYDNEY. [*Received, September* 16*th*, 1921.]

CCV.—*The Dimorphism of Potassium Ethyl Sulphate.*

By DALZIEL LLEWELLYN HAMMICK and JOHN MYLNE MULLALY.

IT was noticed by one of us (J. M. M.) that potassium ethyl sulphate is dimorphous. On crystallisation from methylated alcohol, the substance first appeared in tufts of long, feathery crystals, which, as the solution cooled, redissolved and gave place to the ordinary foliated form. The same dimorphic change was observed after crystallisation from water. In this case, however, the change was suspended for twenty-four hours, the preparation being left untouched and protected from dust. On exposing the mass of crystals to the air, the transformation immediately started at several nuclei and was complete in a few minutes.

In order to show that the change is not one of hydration, the solid phase stable at low temperatures (the α-form) was analysed: 0·5050 gram was heated strongly in a platinum crucible with a few drops of concentrated sulphuric acid until no further decrease in weight occurred. The residue of potassium sulphate weighed 0·2682 gram. Since 0·5050 gram of potassium ethyl sulphate is theoretically equivalent to 0·2680 gram of potassium sulphate, the α-potassium ethyl sulphate cannot be hydrated. This result agrees with the previously published descriptions. Now the β-form can be obtained from the α by crystallisation from absolute alcohol or water, or by merely heating when dry. Hence the β-form must be anhydrous also.

For these and all following experiments the potassium ethyl sulphate was used only after being crystallised from alcohol, and dried in a vacuum over calcium chloride. It was then almost pure, containing only a trace of carbonate.

We are indebted to Mr. T. V. Barker for the following account of the modification stable at higher temperatures:

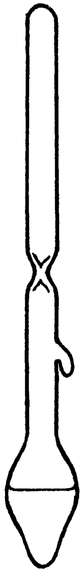
"The higher-temperature modification crystallises in needles with straight extinction, and therefore probably belongs to the orthorhombic system. The faster ray (that is, that with the greater refractive index) vibrates along the axis of elongation.

"The crystals belonging to the previously known monoclinic form are rhombs of about 93° and exhibit diagonal extinction. This is in full agreement with the published description." (See Groth, "Chemische Krystallographie," vol. III, p. 120).

The solubility curves were determined in order to find the transition point. The method used was that of Hartley and Thomas (T., 1906, **89**, 1013).

Known weights of potassium ethyl sulphate (1 to 2·5 grams) mixed with various amounts of water were heated in sealed tubes (see Fig. 1) placed in a bath the temperature of which could be altered at will and read with a standardised thermometer. The last few crystals to dissolve were watched with a lens in order to see whether their edges were rounded (indicating that they were dissolving) or sharp (growing). The required temperature of saturation was then the mean between the highest at which they were seen to grow and the lowest at which they dissolved. It was easy to see which was the solid phase in equilibrium with the solution at different temperatures. Hence the two corresponding solubility curves were obtained intersecting at the transition point, which could only be found thus to be in the neighbourhood of 50°.

FIG. 1.



By dissolving the last trace of solid and then cooling the tube carefully, it was possible to crystallise the β-form at temperatures at which the α was the more stable. Hence a metastable solubility curve was obtained for the β-form. No matter at what temperature crystallisation took place, the β-form was always the first to separate out, and at low temperatures it was much less liable to change to the stable form than at higher ones near the transition point. Great supersaturation of both forms also occurred. In order therefore to induce crystallisation or transformation in the tubes, a small crystal for seeding was placed in the small pocket blown on the stem of the tube (Fig. 1).*

The tubes were cleaned before use by washing with acid, steaming for several hours, and then drying.

The data from which the curves were constructed are as follows :

Percentage of $KC_2H_5SO_4$ in the solution.	Solution temperature for α-form.	Solution temperature for β-form.
49·5	−4·5°	−13·5°
51·946	−1·9	—
58·81	+8·7	− 5·2
66·6	21·1	+12·1
70·015	26·6	20·1
75·29	35·0	32·0
75·675	35·9	32·6
77·99	39·9	38·2
80·084	45·5	45·0
82·04	51·14	51·10
84·44		59·46
84·52		60·46
85·47		65·8
86·23		69·1
87·945		81·3
89·62		91·2

These points when plotted give the curves shown in Fig. 2. The metastable curves are dotted.

The transition point was more accurately determined by the thermometric method. The solid potassium ethyl sulphate was mixed with a small quantity of water contained in a jacketed tube immersed in a water-bath. Both substance and bath were stirred and well-marked arrests in the former's temperature were observed at 51·4°, 51·6°, 51·8°, and 51·8° respectively. More solid was added between each determination, and since this addition caused no further alteration in the value after the third determination, the transition point may be taken as 51·8°.

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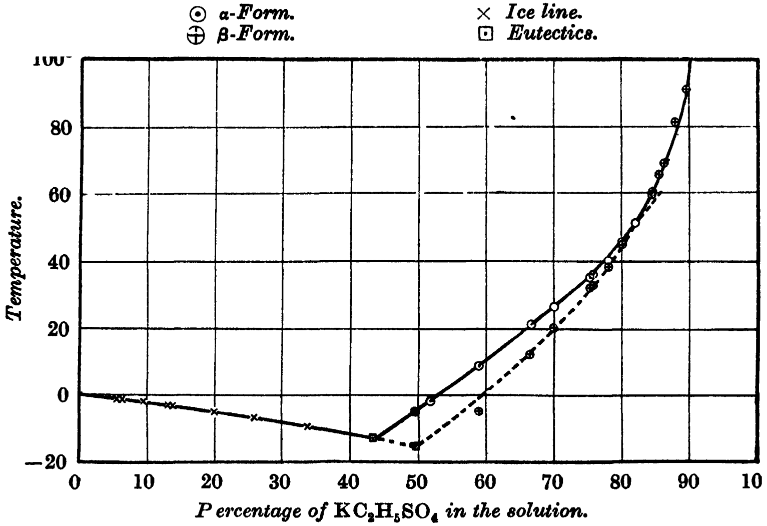
* This device was suggested by General H. B. Hartley.

FIG. 2.

The System: Potassium Ethyl Sulphate–Water.



In order to complete the diagram representing the systems of potassium ethyl sulphate and water, the ice line was determined. The depressions of the freezing point of water by various amounts of the dissolved salt were found by the Beckmann method. The results are given in the following table:

Percentage of $KC_2H_5SO_4$ in the solution.	Freezing point.	Percentage of $KC_2H_5SO_4$ in the solution.	Freezing point.
5·480	−1·195°	13·770	−3·220°
6·370	−1·42	19·808	−4·93
9·434	−2·130	25·953	−6·68
12·953	−2·98	33·714	−9·55

The curve is plotted in Fig. 2, and agrees with that given by Illingworth and Howard (*Phil. Mag.*, 1884, **18**, 123).

The direct determination of the cryohydric points, both stable and metastable, was carried out by cooling a concentrated solution. After ice or potassium ethyl sulphate had ceased separating out alone, and the composition and temperature of the remaining solution had attained those of the eutectic, subsequent solidification took place at constant temperature. This constant temperature was taken as the cryohydric point.

The values obtained for the α-eutectic point were —12·8° and —13·0°. These agree with the extrapolated value, but not with that given by Illingworth and Howard.

The β-eutectic (metastable) was observed first at —15·1° to —15·3° and then at —15·2°.

The mean values are therefore: for the α-eutectic —12·9°, and for the β —15·2°.

We conclude by expressing our gratitude to Brig.-Gen. H. B. Hartley for his valuable help and advice.

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CCVI.—*The Friedel-Crafts' Reaction. Part III. Migration of Alkyl Groups in the Benzene Nucleus.*

By MAURICE COPISAROW.

THE chemical metabolism brought about by the action of aluminium chloride on alkylated hydrocarbons of the aromatic series results in profound molecular rearrangements.

The scission of alkyl groups in the benzene series by means of aluminium chloride was first recorded by Gustavson (*Bull. Soc. chim.*, 1878, [ii], **30**, 22), and by Friedel and Crafts (T., 1882, **41**, 116).

Further work by Friedel and Crafts (T., 1885, **48**, 674), Anschutz and Immendorf (*Ber.*, 1885, **18**, 657), and Heise and Tohl (*Annalen*, 1892, **270**, 168) indicated that the action of aluminium chloride results in a general migration of alkyl and, to a smaller extent, of phenyl groups, with the formation of isomerides, higher and lower alkyl derivatives of benzene, and members of the diphenyl group.

In the light of the investigations of Friedel and Crafts (*Compt. rend.*, 1885, **100**, 692), Hamer (*Proc. Camb. Phil. Soc.*, 1911, **16**, 65), Schröeter (*Brennstoff Chem.*, 1920, **1**, 39), Zanetti and Kindal (*J. Ind. Eng. Chem.*, 1921, **13**, 208, 358), and Copisarow (this vol., p. 442) the action of aluminium chloride appears to extend beyond the migration of groups and results in pyrogenic-like fission of the benzene nucleus with the formation of members of the naphthalene, anthracene, and probably phenanthrene series. The action of ferric chloride on alkyl derivatives of benzene results, not only in migration, but also in chlorination (Thomas, *Compt. rend.*, 1898, **126**, 1213).

In the course of the present investigation the following facts were established :

(1) The action of aluminium chloride on methylated benzene represents qualitatively a reversible reaction in so far as the migration of the alkyl groups is concerned, and, therefore, in this respect it lends itself to the same treatment as is applied in the migration of the halogen atoms (Copisarow, *loc. cit.*).

(2) The fission of the benzene nucleus is facilitated by high temperatures, concentration of aluminium chloride, extent of alkylation of the hydrocarbon, and extension of the period of reaction beyond the maximum required for the migration.

The optimum conditions for the migration were attained by modifying the conditions of reaction in the light of these observations, and also the observations made by Jacobson (*Ber.*, 1885, **18**, 338) and by Anschutz and Immendorf (*Annalen*, 1886, **235**, 177) on the influence of hydrogen chloride.

The increased migration is clearly illustrated by comparison of the 22·9 and 23·7 per cent. yields of toluene from xylene obtained in the present case with that of 12·5 per cent., the maximum found by Fischer and Niggemann (*Ber.*, 1916, **49**, 1475).

The rôle of hydrogen chloride in the reaction consists in its action on the double compound formed by the hydrocarbons with aluminium chloride. Its effect may be expressed by the equations :

$$(1)\ C_6H_5{\cdot}CH_3 + Al_2Cl_6 = C_6H_5{\cdot}Al_2Cl_5 + CH_3Cl.$$
$$(2)\ C_6H_5{\cdot}CH_3 + CH_3Cl = C_6H_4(CH_3)_2 + HCl.$$
$$(3)\ C_6H_5{\cdot}Al_2Cl_5 + HCl = C_6H_6 + Al_2Cl_6.$$

The influence of nitrogen is merely mechanical, whilst the chemical effect of hydrogen is probably due to its action on the methyl chloride formed in the course of the reaction.

The duration of heating was regulated in the experiments carried out in distillation apparatus by the rate of distillation of the products of low b. p.

The limitations of the progress of migration must be attributed to the deteriorating effect of the fission products upon the active surface of the aluminium chloride, rather than to the formation of the fission products as such.

EXPERIMENTAL.

[With CYRIL NORMAN HUGH LONG.]

The Action of Aluminium Chloride on Toluene.

Series I.—Mixtures of toluene (5 parts) and finely powdered aluminium chloride (1 part) were heated on the steam-bath for eight hours under reflux, in one case in presence of a current of nitrogen and in the other of hydrogen chloride at the approximate rate of 3 bubbles per second.

The mixtures gradually darkened with the formation of a deep-red double compound of aluminium chloride with the hydrocarbons present. The reaction mixtures were subsequently treated with ice and a little hydrochloric acid and distilled in a current of steam. The oily layer of the distillate was removed, dried over sodium sulphate, and fractionally distilled, the following fractions being collected: (*a*) up to 100°, (*b*) 100—125°, (*c*) 125—155°, and (*d*) above 155°. On carefully refractionating and comparing these distillates with known mixtures of benzene, toluene, and xylene fractionated in the same apparatus, the following results were obtained:

	Yield per cent. of the theoretical.	
	In nitrogen.	In hydrogen chloride.
Benzene	8·0	11·5
Toluene	90·5	60·0
Xylene (b. p. 136—143°)	7·0	5·3

The calculation of yields was based on the equation:

$$2C_6H_5{\cdot}CH_3 = C_6H_6 + C_6H_4(CH_3)_2.$$

The fractions of high b. p. consist mainly of polyalkylbenzenes, whilst the small quantities of dark tarry residues left after distillation with steam represent the bulk of the products of fission.

In view of the work of Friedel and Crafts (*loc. cit.*), Anschutz and Immendorf (*loc. cit.*), and Copisarow (*loc. cit.*) no effort was made either to separate the polyalkylbenzenes, constituting the fraction of high b. p., or to isolate the complex mixture of hydrocarbons of the tarry residue.

Series II.—Mixtures of toluene and aluminium chloride, in proportions as above, contained in distillation flasks, were heated in presence of currents of nitrogen, hydrogen, and hydrogen chloride, the feature of these experiments being the removal of the products of low b. p., immediately they were formed, from the reaction media.

The temperature, duration of reaction, and method of working up were similar to those employed in series I.

The following results were obtained :

	Yield per cent.		
	In nitrogen.	In hydrogen.	In hydrogen chloride.
Benzene (before and after working up)	14·2	20·8	25·9
Toluene	63·0	77·0	57·8
Xylenes	5·7	8·0	6·5

The fractions of high b. p. and the tarry residue, especially the former, were very small in the experiment carried out in presence of hydrogen.

Series III.—A mixture of toluene (100 parts) and aluminium chloride (3 parts), contained in a distillation flask, was heated in presence of a current of hydrogen chloride, the experimental conditions being identical to those adopted in series II.

The following results were obtained :

Benzene	22·0 per cent. of the theoretical
Toluene	74·2 „ „ „
Xylenes	17·8 „ „ „

The quantity of other products was small.

The Action of Aluminium Chloride on Commercial Xylene.

The xylene employed in the subsequent experiments was prepared by washing crude commercial xylene with a little (6 per cent.) cold concentrated sulphuric acid, with sodium hydroxide, and with water, then drying over sodium sulphate and fractionally distilling, the fraction boiling at 136—143° being utilised.

Series I.—Mixtures of purified commercial xylene (5 parts) with finely powdered aluminium chloride (1 part), contained in a distillation flask, were heated for eight hours in presence of a current of hydrogen chloride.

Experiments were carried out at 100° and 120°. The features of the reaction were similar to those of toluene.

The product of reaction, after treatment with ice and hydrochloric acid, was deep green and showed distinct fluorescence.

The following results were obtained on fractionation of the distillate in a manner identical to that adopted in the previous experiments.

	Yield per cent.	
	At 100°.	At 120°.
Benzene (before and after steam distillation)	7·7	4·1
Toluene „ „ „ „	23·7	16·3
Xylenes (b. p. 136—143°)	45·8	37·0

calculated on the basis of the equations :

$$2C_6H_4(CH_3)_2 = C_6H_5{\cdot}CH_3 + C_6H_3(CH_3)_3 \text{ and}$$
$$2C_6H_4(CH_3)_2 = C_6H_6 + C_6H_2(CH_3)_4$$

although some of the benzene formed may have been due to the action of aluminium chloride on the hydrocarbons produced during the reaction. The residue left after steam-distillation was a viscous, dark-green tar.

Series II.—A mixture of xylene (100 parts) and aluminium chloride (3 parts) was heated at 120° under conditions identical to those of series I.

The product of reaction was pale green, and when subjected to distillation with steam, left but a small tarry residue. The following results were obtained on fractionating the distillate :

Benzene	3·8 per cent. of the theoretical
Toluene	22·9 ,, ,, ,,
Xylenes	50·4 ,, ,, ,,

The complexity and relative quantities of the fractions of high b. p. and residues may be seen from the table given below, 212 grams (2 gram-mols.) of xylene being employed in each experiment.

	Series I.		Series II.
Fraction.	At 100°.	At 120°.	At 120°.
143—162°	10·4 grams	9·8 grams	30·4 grams
162—185°	42·0 ,,	16·3 ,,	35·4 ,,
185—195°	4·8 ,,	4 ,,	2·6 ,,
195—270°	5·2 ,,	4 ,,	3 ,,
Residue (tar)	20 ,,	78 ,,	4 ,,

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CCVII.—*Derivatives of* 3-*Oxy*(1)*thionaphthen.*

By SAMUEL SMILES and ERNEST WILSON MCCLELLAND.

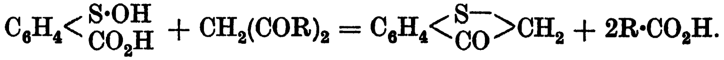
THE experiments described in the following pages are the outcome of a previous investigation of the reactions of aromatic mercaptans in sulphuric acid solution. In this medium oxidation of the mercaptan takes place, disulphides being formed; the properties of the solution indicate that the disulphide is in equilibrium with the mercaptan and sulphenic acid :

$$R{\cdot}S{\cdot}S{\cdot}R \rightleftharpoons R{\cdot}S{\cdot}OH + R{\cdot}SH.$$

The presence of the sulphenic acid has been inferred from the reactions of these solutions. By the addition of other compounds which contain hydrogen available for removal in the form of water, various types of sulphides have been isolated from them :

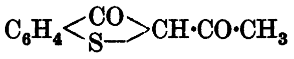
$$R{\cdot}S{\cdot}OH + HR' = R'{\cdot}S{\cdot}R + H_2O.$$

In the case of 2-thiolbenzoic acid and the corresponding disulphide it has been shown that aromatic compounds yield the thioxanthones and that aliphatic compounds containing the ketomethylene group furnish derivatives of 3-oxy(1)thionaphthen; for example, malonic acid or ethyl acetoacetate (T., 1912, **101**, 572) yielded this substance:



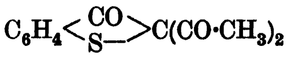
$$C_6H_4{<}\genfrac{}{}{0pt}{}{S\cdot OH}{CO_2H} + CH_2(COR)_2 = C_6H_4{<}\genfrac{}{}{0pt}{}{S-}{CO}{>}CH_2 + 2R\cdot CO_2H.$$

In simple cases such as these the groups R·CO· were found to be eliminated during the condensation, in fact in only one case, that of benzoylacetone, from which 2-benzoyl-3-oxy(1)thionaphthen was obtained, did the product contain the ketonic group of the original substance. The study of this type of reaction was interrupted and a somewhat incomplete account of the results was published (Smiles and Ghosh, T., 1915, **107**, 1378). The experiments which are now described were carried out primarily with the object of obtaining further evidence that derivatives of 3-oxy(1)thionaphthen with substituents in position 2 are formed in the earlier stages of the reaction. This evidence has been obtained in two ways: either by employing milder conditions of reaction which permit these substitution products to escape decomposition, or by choosing material which furnishes characteristic derivatives of greater stability.



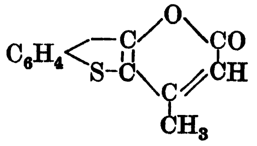
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S-}{>}CH\cdot CO\cdot CH_3$$

(I.)



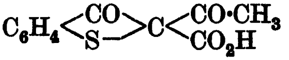
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S-}{>}C(CO\cdot CH_3)_2$$

(II.)



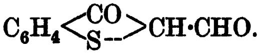
(III.)

In previous experiments with the condensation of 2-thiolbenzoic acid and acetylacetone the formation of 3-oxy(1)thionaphthen was recorded (Smiles and Ghosh, *loc. cit.*). By repeating the process at lower temperatures 2-acetyl-3-oxy(1)thionaphthen (I) has now been obtained in good yield, but the diacetyl derivative (II), which is no doubt the primary product, could not be isolated. In the case of ethyl acetoacetate it has been shown (T., 1912, **101**, 572; 1915, **107**, 1379) that with 2-thiolbenzoic acid and sulphuric acid at 90° "thioindigo," small amounts of oxythionaphthen, and the methylcoumarin (III) are formed. Further experiments carried out at lower temperatures have yielded none of these, but instead gave a product which from its general properties appears without doubt to be the acid (IV). This substance proved too unstable for isolation in a state fit for analysis; oxythionaphthen, in place of the 2-acetyl derivative as expected, being formed from it by hydrolysis with alkaline or acid media or even by mere recrystallisation.



$$C_6H_4<\substack{CO\\S}>C<\substack{CO\cdot CH_3\\CO_2H}$$

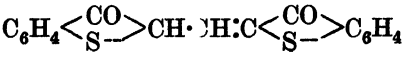
(IV.)



$$C_6H_4<\substack{CO\\S}>CH\cdot CHO.$$

(V.)

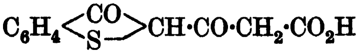
According to the work of von Pechmann (*Ber.*, 1884, **17**, 932), the solution of malic acid in sulphuric acid may be used for generating malonic semialdehyde in the production of coumarins from phenols. This solution also undergoes reaction with 2-thiolbenzoic acid, yielding the 3-oxy(1)thionaphthen-2-aldehyde (V). The aldehyde acid would appear to be formed in the first stage of the process before loss of carbon dioxide takes place; but the amount of the aldehyde met with is quite small, the chief product being the red dyestuff (VI) which is formed from it by the action of sulphuric acid (Friedländer, *Ber.*, 1911, **44**, 3100).



$$C_6H_4<\substack{CO\\S}>CH\cdot CH:C<\substack{CO\\S}>C_6H_4$$

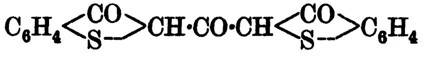
(VI.)

The reaction of 2-thiolbenzoic acid with acetonedicarboxylic acid or with citric acid in sulphuric acid solution has also been studied. The presence of two methylene groups in acetonedicarboxylic acid suggests the possibility that this might unite with one or two molecules of the mercaptan according to the proportions of the reagents present, yielding after loss of carbon dioxide the following substances (VII or VIII):



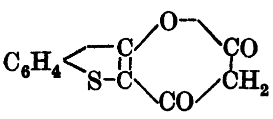
$$C_6H_4<\substack{CO\\S}>CH\cdot CO\cdot CH_2\cdot CO_2H$$

(VII.)



$$C_6H_4<\substack{CO\\S}>CH\cdot CO\cdot CH<\substack{CO\\S}>C_6H_4$$

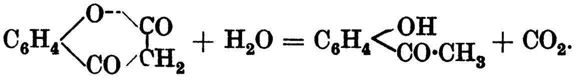
(VIII.)



(IX.)

3-Oxy(1)thionaphthen yields the methylcoumarin (III) on treatment with ethyl acetoacetate in presence of sulphuric acid and, bearing in mind the stability of this coumarin, it must be expected that if a product of type VII were formed, it should be converted by loss of water to the oxycoumarin (IX). This substance has been obtained from the reaction of acetonedicarboxylic acid with 2-thiolbenzoic acid, in fact it appears to be the sole product; a substance derived from type VIII has not been isolated even when excess of the mercaptan was taken.

The structure assigned to this product has been proved by the isolation of the thionaphthen nucleus with the acetyl group derived from the oxycoumarin complex, and by the fact that the substance possesses the characteristic properties of benzotetronic acid (X), or 4-oxycoumarin, which it closely resembles. By distillation with a current of steam the compound yields, with loss of carbon dioxide and absorption of the elements of water, 2-acetyl-3-oxy(1)thionaphthen (I). The constitution of the latter substance is determined by (1) the synthesis from acetylacetone as described in a foregoing paragraph, (2) the conversion to "thioindigo" by alkaline ferricyanide, and (3) the formation of a phenylhydrazone. Moreover, the coumarin derivative is soluble in aqueous sodium carbonate solution; it yields a nitroso-derivative, and on treatment with formaldehyde furnishes the corresponding methylene-bisthionaphthaoxycoumarin. These properties are in close accord with those assigned to benzotetronic acid by Anschutz (*Annalen*, 1909, **367**, 169; 1911, **379**, 333), who recorded the formation of the nitroso- and bismethylene derivatives and the hydrolysis by alkali hydroxide with formation of 2-hydroxyacetophenone:



$$C_6H_4{<}^{O-CO}_{CO-CH_2} + H_2O = C_6H_4{<}^{OH}_{CO\cdot CH_3} + CO_2.$$

(X.)

From the experiments which have now been made on this subject, it is clear that the reaction between 2-thiolbenzoic acid and substances containing the ketomethylene group is of fairly wide application. In all the cases examined the formation of derivatives of 3-oxy(1)thionaphthen has been shown, and from the evidence collected there is little doubt that the 2-derivatives of this substance are the primary products, which, under certain conditions, such as high temperature, may suffer decomposition, yielding the parent oxythionaphthen.

EXPERIMENTAL.

1. *Ethyl Acetoacetate and 2-Thiolbenzoic Acid* (compare T., 1912, **101**, 572).—Twelve grams of ethyl acetoacetate were slowly added to a mixture of 10 grams of 2-thiolbenzoic acid and 120 grams of concentrated sulphuric acid. The solution was continually shaken during the addition of the ester, and the temperature was maintained at 28—30°. The reaction progressed with evolution of sulphur dioxide and solution of the dithiobenzoic acid; it was complete in

about thirty-five minutes. The mixture was then poured over crushed ice and the yellow solid was collected and washed with water. The filtrate contained a small quantity of oxythionaphthen. The solid material proved to be very unstable, being easily resolved into oxythionaphthen; it was obtained in the crystalline state, but still impure, by the slow addition of water to the solution in alcohol. It is soluble in aqueous sodium carbonate, and when heated it decomposes rapidly with effervescence. When treated with a current of steam in presence of a little dilute sulphuric acid, the substance yielded 2-oxy(1)thionaphthen and a considerable quantity of "thioindigo." From 10 grams of thiolbenzoic acid 5 grams of oxythionaphthen were isolated. Hydrolysis may also be effected by dilute aqueous ammonia. The methylcoumarin isolated in previous experiments was not observed in the product formed under these conditions.

2. *2-Acetyl-3-oxy*(1)*thionaphthen* (formula I).—This substance was prepared from the thionaphthacoumarin derivative described in a subsequent paragraph, and by the action of acetylacetone on 2-thiolbenzoic acid.

(*a*) The crude thionaphthoxycoumarin obtained from the interaction of citric acid and 2-thiolbenzoic acid was treated with a current of steam in presence of a little dilute sulphuric acid. The first portion of the distillate contained oxythionaphthen which had been formed during the preparation of the coumarin derivative by the action of hot concentrated sulphuric acid on that substance. The solid which separated from the subsequent distillate was collected and recrystallised from aqueous alcohol; 2-acetyl-3-oxy(1)thionaphthen was thus obtained in pale yellow needles which melted at 81°. The substance is very soluble in most organic media and sparingly so in water (Found: $C = 62{\cdot}1$; $H = 4{\cdot}2$; $S=16{\cdot}9$; $M = 186$. $C_{10}H_8O_2S$ requires $C = 62{\cdot}45$; $H = 4{\cdot}19$; $S = 16{\cdot}69$ per cent.; $M = 192$). The addition of ferric chloride to the alcoholic solution produces a green colour. With hot concentrated sulphuric acid "thioindigo" is slowly formed and the same substance is readily obtained by the addition of potassium ferricyanide to the alkaline solution.

The *phenylhydrazone* of 2-acetyl-3-oxy(1)thionaphthen was prepared by boiling an alcoholic solution of the components for three hours. The crude product was recrystallised by the addition of water to the alcoholic solution; the pure substance formed slender, reddish-brown needles which melted at 131° (Found: $N = 10{\cdot}0$. $C_{16}H_{14}ON_2S$ requires $N = 9{\cdot}9$ per cent.). The scarlet sodium salt of this hydrazone is sparingly soluble in water.

(*b*) Five grams of 2-thiolbenzoic acid were suspended in 50 c.c.

of concentrated sulphuric acid; 3·3 grams of acetylacetone were then gradually added to the mixture, which was kept at 40° for three-quarters of an hour. The solid material obtained by pouring this mixture over crushed ice was washed with water and then treated with a current of steam. The volatile product, after recrystallisation from aqueous alcohol, was identical with that obtained in the foregoing preparation; samples of the phenylhydrazone prepared from the two sources also were identical.

3. 3-*Oxy*(1)*thionaphthen*-2-*aldehyde* (formula V).—A mixture of 10 grams of 2-thiolbenzoic acid and 100 c.c. of concentrated sulphuric acid was heated rapidly to 90°; 15 grams of finely powdered malic acid were then added in the course of fifteen minutes, the contents of the vessel being constantly shaken. After remaining at 90° for another period of fifteen minutes, the mixture was rapidly cooled and then poured over ice. The solid material was collected and thoroughly washed with water; then the aqueous filtrates were shaken with ether, and the solid remaining after this solvent had been evaporated was treated with a current of steam. After recrystallisation, the volatile product melted at 107° (Found: S = 18·1. Calc., S = 18·0 per cent.). It reduced an ammoniacal solution of silver oxide, imparted a green colour to an alcoholic solution of ferric chloride, and with dilute sulphuric acid readily yielded the red dyestuff (formula VI). In all these properties the substance entirely agrees with the 3-oxy(1)thionaphthen-2-aldehyde previously prepared by Friedländer (*loc. cit.*) from " 2-thionaphthen-3-indole-indigotin " (3′-indoxyl-2-thionaphthen-3-one) with sodium ethoxide. The phenylhydrazone was prepared (Found : N = 10·4. Calc., N = 10·4 per cent.), it melted at 136—137°; Friedländer gives 137° as the melting point of this substance. The yields of the aldehyde in this process are very poor, but this is not surprising, since in presence of mineral acids it is readily converted (Friedländer, *loc. cit.*) to the red condensation product. This substance forms the chief product of the reaction now described; it was obtained from the solid material by extraction with a hot dilute solution of sodium hydroxide.

4. (1)*Thionaphtha*-4-*oxycoumarin* (formula IX).—A mixture of 5 grams of 2-thiolbenzoic acid and 12 grams of acetonedicarboxylic acid was added to 50 c.c. of concentrated sulphuric acid. The reaction which set in immediately was completed by keeping the solution at 40—50° for one and a half hours. When the evolution of sulphur dioxide had ceased, the mixture was poured over ice, and the precipitated solid was collected and washed until free from acid. It was then recrystallised from aqueous alcohol, when (1)thionaphtha-4-oxycoumarin was obtained in faintly yellow

needles which melted and decomposed at about 275° (Found: C = 60·1; H = 2·9; S = 14·7. $C_{11}H_8O_3S$ requires C = 60·51; H = 2·77; S = 14·7 per cent.). The substance is insoluble in water and soluble in aqueous sodium hydroxide or carbonate. The action of sodium nitrite yields a yellow nitroso-derivative. The same material is readily prepared by substituting 15 grams of citric acid for the acetonedicarboxylic acid mentioned in the foregoing preparation; at the same time the amount of sulphuric acid should be increased to 80 c.c., but the temperature quoted should not be exceeded, otherwise oxythionaphthen is formed by decomposition of the coumarin derivative. The formation of 2-acetyl-3-oxy(1)thionaphthen from this substance by treatment with steam is described in a foregoing paragraph.

Methylene bis-(1)*thionaphtha-*4-*oxycoumarin* was prepared by the action of formaldehyde upon this coumarin derivative. The substance was easily obtained in the pure condition by adding the calculated quantity of 40 per cent. aqueous formaldehyde to a solution of the naphthacoumarin in alcohol. The mixture was then set aside in a stoppered flask, when the desired substance was gradually precipitated in the crystalline state. The material was collected and the adherent components were removed by boiling alcohol (Found: C = 61·3; H = 3·0; S = 14·3. $C_{23}H_{12}O_6S_2$ requires C = 61·57; H = 2·69; S = 14·3 per cent.). The substance is insoluble in water and most organic media; it dissolves in hot nitrobenzene, from which it separates in small, yellow needles; these melt and decompose at about 300°.

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CCVIII.—*A New Method for the Resolution of Asymmetric Compounds.*

By AKIRA SHIMOMURA and JULIUS BEREND COHEN.

THE production of optically active substances in the living organism is attributed in certain cases to their synthesis in association with active protein or other active constituent of the body. If this is the case, a substance which is already asymmetric in structure would probably yield an active product, that is, a preponderance of one of the active constituents of the mixture, if the asymmetric group were to undergo substitution in combination with active material. Such a process would represent, in the usual acceptation of the term, a modified form of asymmetric synthesis; but as the original molecule, although inactive, has an asymmetric structure, we prefer to call it a new method for the resolution of asymmetric compounds. Thus, supposing an inactive mixture *C*(*abcd*) be combined with an active group, and under such asymmetric conditions *d* be replaced by *e*, yielding *C*(*abce*), then, according to the above principle, the latter compound, when separated from the active group, should exhibit, in a greater or less degree, optical activity.

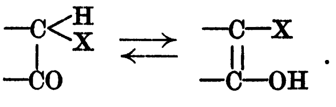
It was with the object of testing the accuracy of this principle that the present research was initiated. The choice of a simple combination between an asymmetric group and an active substance appeared to be limited to the esters of an asymmetric acid with an active alcohol, or to an amide of a similar acid with an active amine. In the first instance, preference was given to the amide combination, as such substances can, as a rule, be hydrolysed by acids without racemisation, whereas hydrolysis of an ester by alkalis may produce inactivity unless great care is exercised. A curious observation was made in the case of certain amides of menthylamine and bornylamine, which were so stable as to resist all attempts at hydrolysis by acids.

The following typical series of substitutions were examined:

$$\underset{\text{(I.)}}{\mathrm{Cl,Br} \xrightarrow{\mathrm{NH_3}} \mathrm{NH_2}};\quad \underset{\text{(II.)}}{\mathrm{Cl,Br} \xrightarrow{\mathrm{M'OH}} \mathrm{OH}};\quad \underset{\text{(III.)}}{\mathrm{OH} \xrightarrow[\mathrm{PCl_5}]{\mathrm{SOCl_2}} \mathrm{Cl}};\quad \underset{\text{(IV.)}}{\mathrm{NH_2} \xrightarrow{\mathrm{HNO_2}} \mathrm{OH}}.$$

The results showed that in the case of I and II, either racemisation occurred or the substance was unchanged, but both III and IV yielded active products.

It is possible that in the first two cases, in which acid radicles containing the group $-\mathrm{CHX{\cdot}CO}-$ ($\mathrm{X = Cl,Br}$) were employed, a form of tautomerism might take place, causing racemisation thus:



$$\begin{array}{l} -\mathrm{C}{<}^{\mathrm{H}}_{\mathrm{X}} \\ \quad | \\ -\mathrm{CO} \end{array} \rightleftarrows \begin{array}{l} -\mathrm{C}-\mathrm{X} \\ \quad \| \\ -\mathrm{C}-\mathrm{OH} \end{array}.$$

We therefore propose to repeat these experiments, using compounds in which hydrogen is not attached to the asymmetric carbon.

The following is a summary of the results: The action of ammonia or water with the addition of silver oxide or sodium carbonate on *l*-menthyl *dl*-phenylchloroacetate, and of ammonia on *l*-menthyl *dl*-phenylbromoacetate and *l*-menthyl *dl*-α-bromo-β-phenylpropionate gave negative results. A similar result was obtained when ammonia was allowed to react with α-bromopropionyl-*l*-tyrosine. Neither phenylchloroaceto-*d*-bornylamide nor the *l*-menthylamide was found suitable for conversion into the amino-compounds.

By the action of thionyl chloride and phosphorus pentachloride on *l*-menthyl *dl*-mandelate and subsequent removal of menthol, active phenylchloroacetic acid was obtained, the product in the first case giving a rotation of $[\alpha]_D^{18}$ − 10°, and in the second $[\alpha]_D^{18}$ − 8·1°.

When *dl*-phenylchloroacetyl-*l*-tyrosine was heated with strong ammonia, and the amino-compound treated with nitrous acid and finally the *l*-tyrosine removed, the mandelic acid, thus obtained, showed a rotation of $[\alpha]^{9}$ + 11·5° in alcoholic solution.

Although the number of positive results are few, they are sufficient to establish the accuracy of the principle, which we hope to extend in a subsequent paper.

EXPERIMENTAL.

Preparation of l-*Menthyl* dl-*Phenylchloroacetate*, $C_6H_5{\cdot}CHCl{\cdot}CO_2{\cdot}C_{10}H_{19}$.

A molecular mixture of *l*-menthol and *dl*-phenylchloroacetyl chloride was heated at 110° for two and a half hours and then at 150° for one hour. The product was extracted with ether. After the ethereal extract had been washed with water and a dilute solution of sodium carbonate, it was dried over sodium sulphate and the ether driven off. The remaining oil was fractionated under diminished pressure and the portion which distilled at 222°/25 mm. (or 220°/22 mm., 210°/18 mm.) collected; 82 per cent. of the theoretical yield was obtained in a favourable case (Found: Cl = 11·66. $C_{18}H_{25}O_2Cl$ requires Cl = 11·49 per cent.). *l*-Menthyl *dl*-phenylchloroacetate, when freshly distilled, is an almost colourless, strongly refracting, viscous oil, having $d_{22^\circ}^{22^\circ}$ 1·070 and $[\alpha]_D^{15^\circ}$ − 68·55° ($\alpha = -22{\cdot}15^\circ$, $l = 0{\cdot}302$).

The oil subsequently solidified to a crystalline mass, melting at 30—41°, after having been kept at the ordinary temperature for eight days. It was easily soluble in alcohol, ether, or light petroleum, but insoluble in water.

Partial resolution of the compound into diastereoisomerides by fractional crystallisation seems to be possible (Wren and Wright, this vol., p. 798). By repeated recrystallisation from alcohol, an ester, having m. p. 34—40° and $[\alpha]_D^{13^\circ}$ − 92·25° ($c = 2$, $l = 2$) in alcoholic solution, was obtained, which on hydrolysis gave a slightly lævorotatory phenylchloroacetic acid.

An attempt to replace the halogen atom of menthyl phenylchloroacetate by the hydroxyl group by the action of cold or hot water, silver oxide, or sodium carbonate was unsuccessful owing to the great stability of the ester towards these agents.

Action of Ammonia on l-*Menthyl* dl-*Phenylchloroacetate.*

Ordinary concentrated ammonia has little action on the compound either at the ordinary temperature or at 100°. The replacement of the chlorine atom by the amino-group was effected to some extent by dissolving the compound in concentrated alcoholic ammonia and maintaining the mixture first at the ordinary temperature for several days and then at 90—100° for about three hours. By the above treatment, in addition to the amino-ester which was formed, a small quantity of the ester was hydrolysed at the same time, menthol being eliminated.

Four grams of *l*-menthyl *dl*-phenylchloroacetate (b. p. 222°/25 mm.) and 50 c.c. of concentrated alcoholic ammonia were placed in a tube, which was then sealed and kept at the ordinary temperature for two days and finally heated at 90—100° for about three hours. The product was carefully evaporated on the water-bath, the residue shaken with ether, dilute hydrochloric acid added, and the mixture again well shaken, whereby the hydrochloride of menthyl phenylaminoacetate was thrown down as a white, flocculent precipitate, which was almost insoluble in cold, but fairly soluble in hot water, from which it crystallised in fine, colourless needles, melting and decomposing at 249°.

The free amino-ester was obtained by adding ammonia to the hot aqueous solution of the hydrochloride and extracting the separated oil with ether. After being kept over-night in an ice-chest, it solidified gradually to a crystalline mass, which, when pressed on a porous plate and recrystallised from alcohol, was obtained in silky needles of m. p. 55° (Found: N = 5·09. $C_{18}H_{27}O_2N$ requires N = 4·84 per cent.). It was soluble in the ordinary organic solvents and showed $[\alpha]_D^{16^\circ}$ − 147·3° ($c = 0{\cdot}930$, $l = 2$) in alcoholic solution.

Menthyl phenylaminoacetate (m. p. 54—55°) could also be obtained directly, in a very poor yield, by passing, from time to time, dry hydrogen chloride through a molten mass of phenylaminoacetic acid in an excess of menthol, which was heated on a water-bath for about eight hours.

In order to hydrolyse menthyl phenylaminoacetate, the compound was dissolved in a slight excess of alcoholic potassium hydroxide (1 c.c. contains 0·016 gram of potassium hydroxide) and kept at the ordinary temperature for five days. The alcohol was evaporated at the ordinary temperature and the residue extracted with warm dilute hydrochloric acid. The filtered acid solution was extracted with ether and then distilled with steam in order to remove any trace of menthol. It was then made slightly alkaline with ammonia, whereby phenylaminoacetic acid was precipitated, which was thoroughly washed with ether to remove any unchanged amino-ester. The phenylaminoacetic acid, thus recovered, melted toward 266°, subliming mostly below that temperature, and showed no appreciable optical activity in dilute hydrochloric acid.

Preparation of l-*Menthyl* dl-*Phenylbromoacetate*, $C_6H_5\cdot CHBr\cdot CO_2\cdot C_{10}H_{19}$.

A molecular mixture of *l*-menthol and *dl*-phenylbromoacetyl bromide was heated at 100—110° for two hours and then at 150° for half an hour. The product was purified as in the case of the chlorine compound. The oil, which distilled at 220—225°/20 mm., solidified to a crystalline mass when kept over-night in the ice-chest. The yield was about 50 per cent. of the theoretical. By repeated recrystallisation from alcohol, the ester was obtained in colourless needles of m. p. 84°, showing $[\alpha]_D^{19°} + 2{\cdot}2°$ ($c = 0{\cdot}68$, $l = 2$) in alcoholic solution (Found: Br = 22·34. $C_{18}H_{25}O_2Br$ requires Br = 22·63 per cent.). The small dextrorotation of the recrystallised product is probably due to partial resolution of the acid radicle. The ester, on hydrolysis, gave a menthol showing $[\alpha]_D^{18°}$ about $- 57°$ in alcoholic solution.

Action of Ammonia on l-*Menthyl* dl-*Phenylbromoacetate.*

Two grams of the bromine compound (b. p. 220—225°/20 mm.) were dissolved in 25 c.c. of concentrated alcoholic ammonia and kept at the ordinary temperature for sixteen days and then finally heated at 80—90° for three hours. The hydrochloride of menthyl phenylaminoacetate (Found: Cl = 11·3. $C_{18}H_{28}O_2NCl$ requires Cl = 10·9 per cent.) melted and decomposed at 245°. The free amino-ester melted at about 55°.

The phenylaminoacetic acid, recovered by hydrolysing the ester with alcoholic potassium hydroxide, was quite inactive in dilute hydrochloric acid.

Preparation of l-*Menthyl* dl-α-*Bromo*-β-*phenylpropionate*, $C_6H_5{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2{\cdot}C_{10}H_{19}$.

A molecular mixture of *dl*-α-bromo-β-phenylpropionyl chloride and *l*-menthol was heated at 100° for two and a half hours and then at 150° for half an hour. The portion which distilled at 212°/15 mm. was collected. The yield was about 76 per cent. of the theoretical. When the oil was kept at the ordinary temperature for a week, it began to solidify in colourless prisms melting at 46—51°. It was obtained in colourless needles of m. p. 50—51° by recrystallisation from alcohol (Found : Br = 21·79. $C_{19}H_{27}O_2Br$ requires Br = 21·76 per cent.). It showed $[\alpha]_D^{14^\circ} - 43{\cdot}8^\circ$ ($c = 2$, $l = 2$) in alcoholic solution.

This compound seems to undergo partial resolution by fractional crystallisation from alcohol, for the compound after crystallisation gave a slightly lævorotatory acid on hydrolysis, whilst that before crystallisation gave an inactive acid by the same treatment.

The compound was acted on by concentrated alcoholic ammonia, the mixture being kept at the ordinary temperature for seven days, and the product was subsequently hydrolysed in the usual way. The amino-acid recovered showed no appreciable activity.

Action of Thionyl Chloride on l-*Menthyl* dl-*Mandelate*.

l-Menthyl *dl*-mandelate was prepared according to the method of McKenzie (T., 1904, **85**, 383). The compound, unlike some compounds of other esters of a similar type, did not undergo any partial resolution by repeated recrystallisation (McKenzie, *loc. cit.*), for the mandelic acid recovered by hydrolysis was quite inactive.

Three grams of *l*-menthyl *dl*-mandelate and 8 grams of thionyl chloride were heated under reflux on a water-bath for two hours. After the excess of the thionyl chloride had been expelled under diminished pressure, the residue was extracted with ether, and the ethereal extract was washed with a dilute solution of sodium carbonate and dried over sodium sulphate. By evaporating the ether, a pale yellow oil was obtained.

In order to hydrolyse the product of chlorination, it was kept at the ordinary temperature for seven days with a slight excess of alcoholic potassium hydroxide. After the alcohol had been evaporated at the ordinary temperature, the residue was made distinctly alkaline with sodium carbonate solution and filtered from some solid matter (chiefly menthol), and any unchanged ester or residual menthol was removed by extraction with ether. The solution was then made acid with hydrochloric acid, whereby phenylchloroacetic acid separated in an oily state. The whole was evaporated down on the water-bath to drive off any trace of menthol. The phenylchloroacetic acid, after being extracted with ether, showed in alcoholic solution $[\alpha]_D^{18°}$ — 10° ($c = 4{\cdot}65$, $l = 2$).

Action of Phosphorus Pentachloride on l-*Menthyl* dl-*Mandelate.*

Five grams of *l*-menthyl *dl*-mandelate and 10 grams of phosphorus pentachloride were heated on the water-bath for five hours and then at 135—140° for one hour. The phosphoryl chloride formed was decomposed by the addition of ice, and the whole was extracted with ether. The ethereal solution, after being dried, gave a certain amount of pale yellow oil. The product of chlorination was hydrolysed as described above, and the phenylchloroacetic acid recovered showed in alcoholic solution $[\alpha]_D^{18°}$ — 8·1° ($c = 3{\cdot}274$, $l = 2$).

Certain bornylamine and menthylamine derivatives of halogenated acids containing an asymmetric carbon atom were prepared, but owing to their striking stability towards hydrolysing agents and to the difficulty in the preparation of their corresponding amino-derivatives, these compounds were found unsuitable for our purpose.

α-*Bromopropiono*-d-*bornylamide*, $C_{10}H_{17}{\cdot}NH{\cdot}CO{\cdot}CHBr{\cdot}CH_3$.

Three grams of *d*-bornylamine hydrochloride were dissolved in 30 c.c. of chloroform and the free base was liberated by the addition of 16 c.c. of *N*-sodium hydroxide. One half of a solution containing 4 grams of α-bromopropionyl bromide in 20 c.c. of chloroform was added to the cold solution of bornylamine, and the mixture was well shaken, the temperature being kept below 0° throughout the reaction. The remaining half of the acid bromide solution was then added, the reaction being kept always slightly alkaline by the occasional addition of sodium carbonate solution. When the reaction was complete, the chloroform layer was separated, and after being dried over sodium sulphate was evaporated as far as possible, and crude α-bromopropiono-*d*-bornylamide was precipitated by the addition of light petroleum. After repeated recrystallisation from dilute alcohol, it was obtained in fine, colourless needles, m. p. 144°, $[\alpha]_D^{15}$ — 29·5° ($c = 1$, $l = 2$) in alcoholic solution (Found : Br = 28·06. $C_{13}H_{22}ONBr$ requires Br = 27·73 per cent.). It was soluble in alcohol, ether, chloroform, or acetone, difficultly soluble in boiling water, but insoluble in cold water or light petroleum.

Phenylchloroaceto-d-*bornylamide*, $C_{10}H_{17}\cdot NH\cdot CO\cdot CHCl\cdot C_6H_5$.

This amide was prepared in the same way as the above compound. By repeated recrystallisation from alcohol, two compounds, one having m. p. 193° and the other m. p. 135°, were obtained. The former showed $[\alpha]_D^{15°}$ $-57{\cdot}0°$ ($c = 1$, $l = 2$) in alcoholic solution (Found: Cl = 11·42. $C_{18}H_{24}ONCl$ requires Cl = 11·60 per cent.), whilst the latter showed $[\alpha]_D^{16°}$ $+2°$ ($c = 1$, $l = 2$) in the same solvent (Found: Cl = 11·80. $C_{18}H_{24}ONCl$ requires Cl = 11·60 per cent.).

Phenylchloroaceto-l-*menthylamide*, $C_{10}H_{19}\cdot NH\cdot CO\cdot CHCl\cdot C_6H_5$.

In this case also two compounds were obtained, one having m. p. 174—175° and the other m. p. 113°, by repeated recrystallisation from alcohol. The former showed $[\alpha]_D^{16°}$ $-113°$ ($c = 0{\cdot}5$, $l = 2$) in alcoholic solution (Found: Cl = 11·39. $C_{18}H_{26}ONCl$ requires Cl = 11·52 per cent.), whilst the latter showed $[\alpha]_D^{16°}$ $-47°$ ($c = 0{\cdot}5$, $l = 2$) in the same solvent (Found: Cl = 11·44. $C_{18}H_{26}ONCl$ requires Cl = 11·52 per cent.).

The existence of two isomerides of the bornylamine and menthylamine derivatives is probably due to resolution of the acid radicle, but as the amides resisted hydrolysis by acids, the point could not be ascertained.

Preparation of dl-α-*Bromopropionyl*-l-*tyrosine*,
$OH\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CHBr\cdot CH_3$.

Following Fischer's method for preparing chloroacetyl-*l*-tyrosine (*Ber.*, 1904, **37**, 2486), a satisfactory yield of α-bromopropionyl-*l*-tyrosine ethyl ester was obtained by treating *l*-tyrosine ethyl ester hydrochloride, having $[\alpha]_D^{12°}$ $-8{\cdot}3°$ ($c = 2$, $l = 2$) in aqueous solution, with α-bromopropionyl bromide in an alkaline medium at a temperature below 0°, using chloroform as a solvent.

α-*Bromopropionyl*-l-*tyrosine ethyl ester* melted towards 131°, after having been twice precipitated from chloroform solution by the addition of light petroleum (Found: Br = 23·46. $C_{14}H_{18}O_4NBr$ requires Br = 23·22 per cent.). It was almost insoluble in cold water, with difficulty in hot water; soluble in alcohol, ether, or chloroform, but insoluble in light petroleum. It gave Millon's reaction and showed $[\alpha]_D^{15°}$ $+12{\cdot}5°$ ($c = 2$, $l = 2$) in alcoholic solution.

Free α-bromopropionyl-*l*-tyrosine was obtained in an oily state by hydrolysing the ethyl ester with a dilute solution of sodium hydroxide at the ordinary temperature, and was found to be identical with that which was prepared directly by the action of α-bromopropionyl bromide on *l*-tyrosine. The compounds obtained by both methods have much higher dextrorotatory power than the ethyl ester showing specific rotation between 30° and 40°.

Action of Ammonia on dl-α-*Bromopropionyl*-l-*tyrosine.*

Three grams of α-bromopropionyl-*l*-tyrosine were dissolved in 20 c.c. of concentrated aqueous ammonia and heated in a sealed tube in a water-bath for five hours. When the contents were evaporated, a syrupy mass was obtained, which, without further purification, was directly hydrolysed by boiling with concentrated hydrochloric acid. After the tyrosine had been removed, the solution, which should contain alanine, was examined polarimetrically, but showed no appreciable activity.

Preparation of dl-*Phenylchloroacetyl*-l-*tyrosine*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CO{\cdot}CHCl{\cdot}C_6H_5$.

The direct synthesis of phenylchloroacetyl-*l*-tyrosine by the action of phenylchloroacetyl chloride on *l*-tyrosine was not successful. Its ethyl ester was therefore prepared in the same way as given above, and by subsequent hydrolysis, the free acid was obtained.

Phenylchloroacetyl-*l*-tyrosine ethyl ester was prepared in a moderate yield, in colourless needles (from alcohol) melting at 140—141° (Found: Cl = 9·87. $C_{19}H_{20}O_4NCl$ requires Cl = 9·80 per cent.). It gave Millon's reaction and showed $[\alpha]_D^{18°}$ + 24° (c = 1·5, l = 2) in alcoholic solution. It was almost insoluble in hot or cold water or light petroleum, but soluble in the other ordinary organic solvents.

Free phenylchloroacetyl-*l*-tyrosine was obtained by hydrolysing the ethyl ester with a dilute solution of sodium hydroxide at the ordinary temperature. It was obtained in small needles, melting towards 125° (Found: Cl = 10·20. $C_{17}H_{16}O_4NCl$ requires Cl = 10·63 per cent.).

It was moderately soluble in hot water, from which it separated in an amorphous state on cooling. It gave Millon's reaction.

Action of Ammonia on dl-*Phenylchloroacetyl*-l-*tyrosine.*

Two grams of the substance were dissolved in 20 c.c. of strong aqueous ammonia and warmed in a sealed tube at 80—90° for three hours. The product of amination, when carefully evaporated, gave a syrupy mass, which was used for the next experiment without further purification.

Action of Nitrous Acid on Phenylaminoacetyl-l-*tyrosine.*

The substance was dissolved in dilute hydrochloric acid and cooled to 0°, and the calculated quantity of sodium nitrite was then added and the mixture well stirred. The reaction was completed by warming on the water-bath for some time.

The product was then mixed with concentrated hydrochloric acid and boiled for two and a half hours under reflux in order to hydrolyse it completely. After the intensely coloured solution had been treated with animal charcoal, it was neutralised with ammonia, whereby tyrosine was precipitated in white, microneedles, showing in 1·22*N*-hydrochloric acid $[\alpha]_{D}^{19^\circ} - 8{\cdot}2^\circ$ ($c = 0{\cdot}669$, $l = 2$).

The filtrate was made distinctly acid by the addition of hydrochloric acid and extracted with ether. The ethereal solution, showing a slight dextrorotatory power, after having been dried over sodium sulphate, was shaken with a dilute solution of sodium hydroxide. The aqueous alkaline solution was again made acid by the addition of hydrochloric acid and finally extracted with ether. The dried ethereal extract, on evaporation, gave a small quantity of mandelic acid (melting towards 110°), which showed $[\alpha]_{D}^{19^\circ} + 11{\cdot}5^\circ$ ($c = 0{\cdot}13$, $l = 2$) in alcoholic solution.

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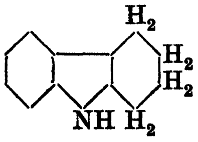
[*Received, September* 16*th*, 1921.]

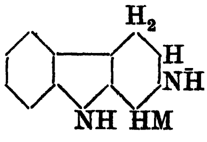
CCIX.—*Derivatives of Tetrahydrocarbazole.*

By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT.

INTEREST attaches to the reduction products of carbazole and particularly to tetrahydrocarbazole (I), in the first place because it is probable that strychnine is a derivative of the latter substance (compare Perkin and Robinson, T., 1910, **97**, 315), and secondly because tetrahydrocarbazole is structurally somewhat closely related to tetrahydroharmine (II) (T., 1919, **115**, 938).



(I.)



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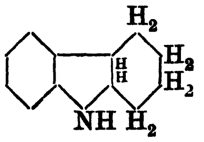


(III.)

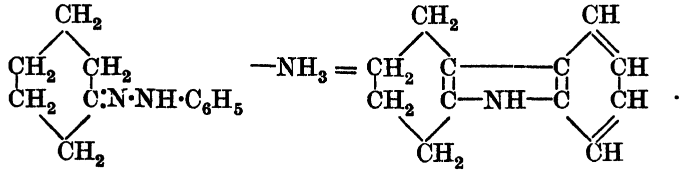
The reduction of carbazole, $C_{12}H_9N$, was first investigated by Graebe and Glaser (*Annalen*, 1872, **163**, 352), who showed that, when heated with hydriodic acid and phosphorus at 220—240°, it attaches six atoms of hydrogen yielding *carbazoline*, $C_{12}H_{15}N$, which is now known to have the constitution (III).

These investigators also showed that carbazoline hydrochloride is decomposed on distillation into hydrogen, hydrogen chloride, and tetrahydrocarbazole (m. p. 120°):

$$C_{12}H_{15}N,HCl = H_2 + HCl + C_{12}H_{13}N.$$

In 1888, Drechsel (*J. pr. Chem.*, 1888, [ii], **38**, 65) submitted phenol to electrolysis with an alternating current and isolated a substance, $C_6H_{10}O$ (b. p. 153—178°), which he named *hydrophenoketone.* Drechsel combined this substance with phenylhydrazine and treated the product with dilute sulphuric acid, when he obtained a substance, $C_{12}H_{13}N$ (m. p. 108°), which he named *hydrophenanilide.* He recognised the fact that this substance had the same composition as Graebe and Glaser's tetrahydrocarbazole, but concluded that the substances were not identical because of the difference in their melting points.

Baeyer (*Ber.*, 1889, **22**, 2185; *Annalen*, 1894, **278**, 105) was the first to point out that Drechsel's hydrophenoketone is identical with *cyclo*hexanone and that hydrophenanilide, in spite of its rather low melting point, is tetrahydrocarbazole. He also pointed out that the conversion of the phenylhydrazone of *cyclo*hexanone into tetrahydrocarbazole is an example of the Fischer indole synthesis and that the change is to be represented thus:



It is somewhat remarkable that this interesting substance has been so little investigated; almost all that is known about its derivatives is due to the work of Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 53). These investigators were unsuccessful in their attempts to nitrate tetrahydrocarbazole (*loc. cit.*, p. 60) and prepared 8-nitro- and 6-nitro-tetrahydrocarbazoles,* m. p. 149° and 174° respectively,

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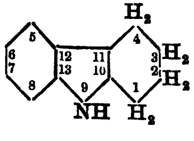
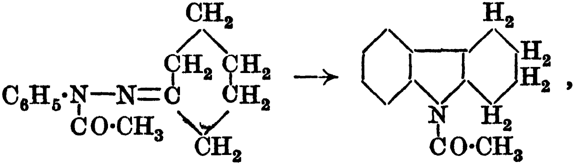
* The scheme of numbering the positions in tetrahydrocarbazole employed in this communication is



from the condensation products of *cyclo*hexanone with *o*- and *p*-nitrophenylhydrazine. In the case of the condensation product of *m*-nitrophenylhydrazine with *cyclo*hexanone they assume that the nitrotetrahydrocarbazole (m. p. 154°) produced by the action of dilute sulphuric acid is the 7-nitro-derivative, although it might well be the 5-nitro-derivative. This question of constitution is discussed in detail below.

The work described in the present communication may be briefly summarised as follows. We find, in the first place, that the phenylhydrazone of *cyclo*hexanone is converted almost quantitatively into tetrahydrocarbazole simply by boiling with glacial acetic acid, and in this and other similar cases the product is much cleaner than that obtained by the usual process, namely, boiling the phenylhydrazones with dilute sulphuric acid. The 9-acetyl derivative of tetrahydrocarbazole (IV, m. p. 78°), is readily obtained either by boiling *cyclo*hexanoneacetylphenylhydrazone with dilute sulphuric acid,



(IV.)

or directly from tetrahydrocarbazole by boiling with acetic anhydride or with acetyl chloride in the presence of copper powder at the ordinary temperature.

Contrary to the experience of Borsche, Witte, and Bothe (*loc. cit.*, p. 60), we find that it is possible to nitrate tetrahydrocarbazole direct if the solution in sulphuric acid is treated with potassium nitrate at — 5°. The sole product is 6-nitrotetrahydrocarbazole melting at 174°, since it is identical with the substance which results from the action of dilute acids on *cyclo*hexanone-*p*-nitrophenylhydrazone. Additional evidence in support of this view of its constitution was obtained in the following way.

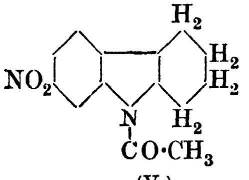
The nitro-derivative, on reduction, yields 6-*aminotetrahydrocarbazole*, which melts at 152° and yields an acetyl derivative melting at 208°, and these substances have been synthesised by the following steps. p-*Acetylaminophenylhydrazine*,

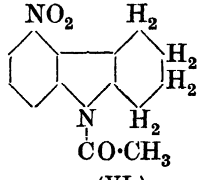
$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2,$$

prepared from *p*-aminoacetanilide by diazotisation and reduction, condenses readily with *cyclo*hexanone, yielding cyclo*hexanone*-p-*acetylaminophenylhydrazone* (m. p. 166°), and this substance, when digested with glacial acetic acid, is converted into 6-*acetylaminotetrahydrocarbazole* (m. p. 208°), which was found to be identical with the derivative of this composition obtained from the product of the nitration of tetrahydrocarbazole. On hydrolysis, it yielded 6-*aminotetrahydrocarbazole* melting at 152°.

Unexpected results were obtained in a series of experiments on the nitration of 9-acetyltetrahydrocarbazole (IV) in acetic acid solution. The product of nitration is a single *acetylnitrotetrahydrocarbazole* which melts at 174° and, on hydrolysis, yields a new *nitrotetrahydrocarbazole* melting at 172°. It was at first thought that the latter was identical with the 6-nitro-derivative (m. p. 174°), but this was shown not to be the case, (i) by a mixed melting point determination, and (ii) by preparing the *acetyl* derivative of 6-*nitrotetrahydrocarbazole*, which was found to melt at 244° instead of 174°.

It is certainly remarkable that the action of nitric acid on the acetyl derivative should lead to the introduction of the nitro-group into a different position from that which it takes up when tetrahydrocarbazole itself is nitrated. With regard to the constitution of the acetyl derivative of the new nitrotetrahydrocarbazole, two formulæ only are possible for reasons given below, namely, V and VI.

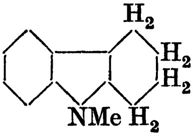

(V.)

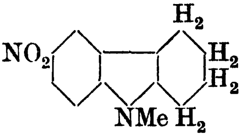

(VI.)

The question has an important bearing on the difficult problem of the nature of the nitrotetrahydrocarbazole which is formed from *cyclo*hexanone-*m*-nitrophenylhydrazone by the action of dilute acids. We have repeated the experiments of Borsche, Witte, and Bothe (*loc. cit.*, p. 68) and have satisfied ourselves that the action of dilute sulphuric acid on this *m*-nitrophenylhydrazone leads to the formation of a single nitrotetrahydrocarbazole (m. p. 154°) and not to a mixture of isomerides. The above-named investigators assign the 7-nitro-structure to this substance, and we are inclined to agree with their view that it is 7-*nitrotetrahydrocarbazole*.

It is, of course, conceivable that the *m*-nitrophenylhydrazone might yield 5-nitrotetrahydrocarbazole, but this, in our view, is probably the constitution of the isomeride which results from the nitration of 9-acetyltetrahydrocarbazole. Unfortunately, the experimental data available at the present time are not sufficient to allow of a decision as to the actual formula either of the product of the nitration of 9-acetyltetrahydrocarbazole or of the nitro-derivative formed from *cyclo*hexanone-*m*-nitrophenylhydrazone by the action of dilute sulphuric acid.

After the unexpected results which have been obtained in the nitration of 9-acetyltetrahydrocarbazole, it was thought that it would be interesting to investigate the nitration of a derivative of tetrahydrocarbazole containing a different radicle attached to the nitrogen atom, and for this purpose, 9-*methyltetrahydrocarbazole* (VII) was selected.

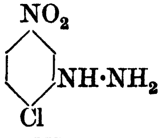

(VII.)

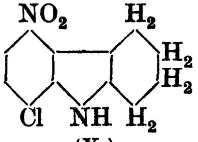

(VIII.)

This substance, which appears to be new, was obtained by combining *as*-phenylmethylhydrazine, $C_6H_5{\cdot}NMe{\cdot}NH_2$, with *cyclo*hexanone and then digesting the resulting cyclo*hexanonephenylmethylhydrazone* with dilute sulphuric acid. 9-*Methyltetrahydrocarbazole* melts at 50° and, on nitration, readily yields 6-nitro-9-methyltetrahydrocarbazole (VIII, m. p. 192°). That the nitro-group in this substance occupies the 6-position was proved in the following way. On reduction, it yields 6-*amino*-9-*methyltetrahydrocarbazole* (m. p. 105°), the acetyl derivative of which melts at 238°. In order to synthesise this substance, *p*-aminomethylaniline was acetylated and the p-*acetylaminomethylaniline* converted into p-*acetylaminonitrosomethylaniline*, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe{\cdot}NO$, by means of nitrous acid. This, on reduction with zinc dust and acetic acid, yielded p-*acetylaminophenylmethylhydrazine*, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe{\cdot}NH_2$, which combined readily with *cyclo*hexanone.

The cyclo*hexanone*-p-*acetylaminophenylmethylhydrazone* was then boiled with glacial acetic acid, when it yielded 6-*acetylamino*-9-*methyltetrahydrocarbazole*, which melted at 238° and proved to be identical with the substance of this composition obtained from the direct nitration of 9-methyltetrahydrocarbazole in the way described above.

During the course of these experiments, we were anxious to ascertain whether the presence of substituents in the 2- and 5-positions in phenylhydrazine would, by steric hindrance, prevent the Fischer indole synthesis from taking place, and we selected for experiment, 2-*chloro*-5-*nitrophenylhydrazine* (IX).


(IX.)


(X.)

This substance, which does not appear to have been described, was made as follows. *o*-Chloroaniline, on nitration in concentrated sulphuric acid solution, yields 2-chloro-5-nitroaniline which, when diazotised and reduced with stannous chloride, is converted into 2-chloro-5-nitrophenylhydrazine (m. p. 160°). This combines readily with *cyclo*hexanone, and the resulting cyclo*hexanone-2-chloro-5-nitrophenylhydrazone* (m. p. 78°) reacts readily with hot dilute sulphuric acid, yielding *8-chloro-5-nitrotetrahydrocarbazole* (X), which crystallises in orange prisms melting at 214°. This rather unexpected result shows that the occupation of the 2- and 5-positions in phenylhydrazine does not inhibit tetrahydrocarbazole formation.

The new carbazole derivatives which have been synthesised during the course of this investigation from *cyclo*hexanone are in all cases derivatives of tetrahydrocarbazole, and it seemed desirable to endeavour to discover some process of oxidation which would remove the additional hydrogen atoms and yield the corresponding derivatives of carbazole. The information thus obtained would also be valuable in deciding the constitution of some nitro- and other derivatives of carbazole as to which there is still some doubt.

Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 75) heated tetrahydrocarbazole and several of its methyl derivatives with lead oxide at a high temperature and obtained small yields of carbazole and the corresponding methyl derivatives, but such a process is obviously inapplicable to the nitro- or halogeno-derivatives of tetrahydrocarbazole. During the investigation of harmine and harmaline, Perkin and Robinson (T., 1919, **115**, 961) showed that tetrahydroharmine, $C_{13}H_{16}ON_2$, is converted into harmaline, $C_{13}H_{14}ON_2$, when it is oxidised with permanganate. We were unsuccessful when we attempted to obtain dihydrocarbazole or carbazole from tetrahydrocarbazole by a similar process. An oxidising agent which has proved valuable in cases of this kind is mercuric acetate, thus, for example, tetrahydroepiberberine is readily oxidised to epiberberine by this reagent with the loss of four atoms of hydrogen (Perkin, T., 1918, **113**, 515). On investigating the behaviour of tetrahydrocarbazole and 9-methyltetrahydrocarbazole towards mercuric acetate, we find that oxidation takes place readily with the formation of carbazole and 9-methylcarbazole, although the yields at present are not good. There are indications that this process may also be successfully applied in the case of halogeno- and nitro-derivatives of tetrahydrocarbazole, and this point is being investigated.

EXPERIMENTAL.

Tetrahydrocarbazole, $C_{12}H_{13}N$ (I).

In preparing this substance, Borsche (*Annalen*, 1908, **359**, 60) combines *cyclo*hexanone with phenylhydrazine and boils the resulting hydrazone with dilute sulphuric acid, but the product obtained in this way is always impure and pink-coloured. We find that a purer product is obtained direct when the hydrazone is boiled for a few minutes with five times its weight of glacial acetic acid, from which it separates, on cooling, as a mass of crystals melting at 119°, whereas Borsche gives 116° as the melting point.

The *picrate* separates, when a hot alcoholic solution of tetrahydrocarbazole is mixed with alcoholic picric acid, in dark red crystals melting at 147°, and recrystallisation from alcohol does not alter this melting point. Padoa and Chiaves (*Atti R. Accad. Lincei*, 1907, [v], **16**, 765) give the melting point of a specimen of the picrate prepared from tetrahydrocarbazole obtained by the reduction of carbazole as 133°, but most probably their tetrahydrocarbazole contained some unchanged carbazole.

9-*Acetyltetrahydrocarbazole* (IV).—The *cyclo*hexanoneacetylphenylhydrazone used in the preparation of this substance was obtained by heating *cyclo*hexanonephenylhydrazone with an equal weight of freshly-distilled acetic anhydride on the steam-bath for two hours and then distilling under reduced pressure, when the acetyl derivative passed over at 210—220°/14 mm. as a viscous liquid which did not crystallise (Found: $N = 12{\cdot}1$. $C_{14}H_{18}ON_2$ requires $N = 12{\cdot}2$ per cent.).

When this acetyl-hydrazone was heated with dilute sulphuric acid (20 per cent.) for a few minutes, an oil resulted which solidified on cooling. This product was recrystallised from alcohol, from which it separated in thick prisms melting at 77°, and this proved to be pure 9-*acetyltetrahydrocarbazole*. In this particular case it was found rather unexpectedly that the closing of the indole ring, by boiling with acetic acid, occurred with some difficulty, and even after boiling for an hour some acetyl-hydrazone remained unchanged. The same acetyl derivative was obtained by the direct acetylation of tetrahydrocarbazole under the following conditions: Tetrahydrocarbazole (30 grams) was mixed with glacial acetic acid (150 c.c.) and acetyl chloride (50 c.c.), and after adding a little copper powder, the whole was allowed to remain for fourteen days in a flask fitted with a calcium chloride tube. The product was decomposed by ice and water, the sticky, dark green solid extracted with chloroform, the extract dried over calcium chloride, the chloroform removed, and the residue distilled under reduced pressure, when an almost colourless distillate was obtained which solidified on cooling. This separated from alcohol in colourless crystals melting at 77°, and proved to be identical with the 9-acetyltetrahydrocarbazole obtained from the acetyl-hydrazone as explained above (Found : N = 6·5. $C_{14}H_{15}ON$ requires N = 6·6 per cent.).

This acetyl derivative may also be obtained by boiling tetrahydrocarbazole with three times its weight of acetic anhydride for six hours and then distilling the product. Several attempts were made to prepare 9-benzoyltetrahydrocarbazole from tetrahydrocarbazole by the action of benzoyl chloride under varying conditions, but the product was always resinous and could not be purified. Similar results were obtained when benzoic anhydride was used. If the solution of tetrahydrocarbazole in glacial acetic acid is boiled with benzoyl chloride in the presence of a little copper powder, and the product distilled, a solid is obtained which after crystallisation melts at 77° and consists of 9-acetyltetrahydrocarbazole.

The Nitration of Tetrahydrocarbazole.

6-*Nitro- and* 6-*Amino-tetrahydrocarbazole.*

It is explained in the introduction (p. 1827) that the nitration of tetrahydrocarbazole may be directly accomplished at low temperatures, and the following conditions have been found to work well :

Tetrahydrocarbazole (10 grams), dissolved in concentrated sulphuric acid (70 c.c.), is cooled to — 5° and then the theoretical quantity (5·9 grams) of powdered potassium nitrate added in small quantities at a time, the solution being continuously stirred and kept below — 3°. The product is poured on to ice, the crude, yellow nitro-compound collected, washed thoroughly with water, and dried over sulphuric acid. It is then recrystallised from alcohol, from which it separates in small, thick prisms melting at 174°, and careful comparison showed that this substance is identical with the nitrotetrahydrocarbazole obtained by Borsche (*Annalen*, 1908, **359**, 67) from *cyclo*hexanone-*p*-nitrophenylhydrazone by warming with sulphuric acid.

The 9-*Acetyl Derivative.*—This substance, which was required for comparison with the acetyl derivative obtained by nitrating acetyltetrahydrocarbazole (compare p. 1828), was prepared in the following manner. 6-Nitrotetrahydrocarbazole (5 grams) was boiled with acetic anhydride (50 c.c.) for two hours, when, on cooling, yellow needles separated, which were recrystallised from glacial acetic acid (Found : N = 10·8. $C_{14}H_{14}O_3N_2$ requires N = 10·8 per cent.).

6-*Nitro-9-acetyltetrahydrocarbazole* melts at 244° and is readily hydrolysed to 6-nitrotetrahydrocarbazole when it is digested with a solution of sodium hydroxide in 50 per cent. aqueous alcohol.

6-*Aminotetrahydrocarbazole.*—In order to prepare this substance, the nitro-derivative (4 grams) was added to a mixture of iron filings (10 grams), water (100 c.c.), and hydrochloric acid (3 c.c.) and the whole heated on the steam-bath for an hour with frequent shaking. The product was cooled, made alkaline with sodium hydroxide, and the solid collected and extracted several times with boiling water, when, on cooling, the amino-derivative separated in crystals, the yield being about 40 per cent. of the theoretical.

6-*Aminotetrahydrocarbazole* separates from alcohol or toluene in colourless plates and melts at 152° (Found: N = 15·1. $C_{12}H_{14}N_2$ requires N = 15·0 per cent.). The picrate was prepared by mixing the hot alcoholic solution of the amino-derivative (1 gram) with picric acid (1·2 grams), when, on cooling, bright red needles separated which, after recrystallisation from alcohol, melted at 214° with decomposition.

6-*Acetylaminotetrahydrocarbazole* was prepared by mixing the amino-derivative in hot benzene with a slight excess of acetic anhydride. The crystalline mass was collected and recrystallised from dilute acetic acid, from which it separated in thick, colourless prisms melting at 208°.

6-*Benzoylaminotetrahydrocarbazole* was precipitated when the amino-derivative, dissolved in hot benzene, was mixed with benzoyl chloride, and separated from alcohol in clusters of short prisms melting at 207° (Found: N = 9·6. $C_{19}H_{18}ON_2$ requires N = 9·7 per cent.).

Synthesis of 6-*Acetylaminotetrahydrocarbazole.*—For the purpose of this synthesis, *p*-acetylaminophenylhydrazine hydrochloride was prepared from *p*-aminoacetanilide by reduction with stannous chloride in the usual manner (Riedel, D.R.-P. 80843) and was employed as such because the free base is difficult to obtain pure and rapidly decomposes on standing in the air. Sodium (5 grams) dissolved in alcohol (80 c.c.) was mixed with *cyclo*hexanone (6·5 grams) and the hydrazine hydrochloride from 10 grams of *p*-aminoacetanilide added, when there was considerable rise of temperature. The whole was warmed on the steam-bath for a few minutes, mixed with water, the precipitate collected and recrystallised from alcohol, from which it separated in needles melting at 165—166°, and this substance, which decomposed gradually on keeping, is cyclo*hexanone*-p-*acetylaminophenylhydrazone* (Found: N = 17·1. $C_{14}H_{19}ON_3$ requires N = 17·1 per cent.). When an attempt was made to convert this substance into the corresponding indole derivative by the action of sulphuric or hydrochloric acid, simultaneous elimination of the acetyl group took place.

It was, however, found that glacial acetic acid leads directly and easily to 6-acetylaminotetrahydrocarbazole. The hydrazone was simply heated with glacial acetic acid almost to the boiling point, the flame was then removed, when the formation of the indole ring took place so energetically that the acid boiled for some time. On the addition of a little water, 6-*acetylaminotetrahydrocarbazole* separated from the dilute acetic acid in short, colourless prisms melting at 208° (Found: N = 12·5. $C_{14}H_{16}ON_2$ requires N = 12·3 per cent.). The free amino-derivative was obtained by boiling the acetyl derivative with concentrated hydrochloric acid for ten minutes, during which time the hydrochloride separated as a gelatinous precipitate. The whole was mixed with ice, made alkaline with ammonia, and the amino-derivative collected, washed, dried, and recrystallised from alcohol, from which it separated in small plates melting at 152°. A careful comparison showed that this base (and its acetyl derivative) is identical with 6-aminotetrahydrocarbazole (and its acetyl derivative) prepared from 6-nitrotetrahydrocarbazole by reduction in the manner described above.

9-*Methyltetrahydrocarbazole* (VII) *and its* 6-*Nitro-* (VIII) *and* 6-*Amino-derivatives.*

9-Methyltetrahydrocarbazole, which does not appear to have been described, may be obtained from *cyclo*hexanone and *as*-phenylmethylhydrazine in the following manner: The phenylmethylhydrazine (5 grams) is mixed with *cyclo*hexanone (4·1 grams), when there is a considerable rise of temperature and the mixture becomes cloudy owing to the separation of water.

After heating on the steam-bath for a few minutes, the hydrazone is converted into the carbazole by boiling with sulphuric acid (20 c.c.) and water (90 c.c.), when an oil separates which crystallises on cooling, and on recrystallisation from alcohol 9-methyltetrahydrocarbazole separates in colourless needles. Alternatively, the hydrazone is boiled with glacial acetic acid for a few minutes, when, on diluting with water, the carbazole separates as an oil which soon solidifies and is again crystallised from alcohol (Found: N = 7·5. $C_{13}H_{15}N$ requires N = 7·6 per cent.).

9-*Methyltetrahydrocarbazole* melts at 50° and yields a picrate which separates from alcohol in dark red needles melting at 116°.

6-*Nitro*-9-*methyltetrahydrocarbazole* was obtained in almost quantitative yield by the method used in the case of the preparation of 6-nitrotetrahydrocarbazole, and the crude product was crystallised from glacial acetic acid, from which it separated in long, yellow prisms melting at 192° (Found: N = 12·2. $C_{13}H_{14}O_2N_2$ requires N = 12·2 per cent.).

6-*Amino*-9-*methyltetrahydrocarbazole* was prepared by reducing the nitro-derivative with iron and a little hydrochloric acid (compare p. 1829), and the product was extracted with boiling water, when, on cooling, the amino-derivative separated in colourless prisms melting at 105°.

The *picrate* crystallises from hot alcohol in orange needles and melts at 212° (Found: N = 16·1. $C_{13}H_{16}N_2,C_6H_2(OH)(NO_2)_3$ requires N = 16·3 per cent.).

6-*Acetylamino*-9-*methyltetrahydrocarbazole* is readily obtained by adding acetic anhydride to the solution of the amino-compound in benzene and is purified by crystallisation from acetic acid, from which it separates in colourless needles melting at 238° (Found: N = 11·6. $C_{15}H_{18}ON_2$ requires N = 11·6 per cent.).

Synthesis of 6-*Acetylamino*-9-*methyltetrahydrocarbazole.*—For the purpose of this synthesis, *p*-aminomethylaniline, $NH_2{\cdot}C_6H_4{\cdot}NHMe$, was prepared by the reduction of *p*-nitrosomethylaniline with sodium sulphide. This was dissolved in benzene and treated with the theoretical amount of acetic anhydride, when there was considerable rise of temperature and *p*-acetylaminomethylaniline separated as an oil. This was extracted and separated from the benzene by the calculated quantity of dilute hydrochloric acid, the solution was cooled below 0°, and the required amount of sodium nitrite, dissolved in a little water, added gradually with continuous stirring. The p-*acetylaminonitrosomethylaniline*, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe{\cdot}NO$, which separated in rather poor yield as a yellow, crystalline mass, was collected, washed with water, and recrystallised from alcohol, from which it separated in almost colourless plates and melted at 146° (Found: N = 21·7. $C_9H_{11}O_2N_3$ requires N = 21·8 per cent.). This acetyl derivative (4 grams) was made into a paste with glacial acetic acid (6 grams) and gradually added to water (21 c.c.) and zinc dust (12 grams of 90 per cent.) with continuous stirring, when there was some rise of temperature, which, however, was kept below 25°.

After remaining over-night, the product was rendered alkaline by the addition of sodium hydroxide, extracted with much ether, the ethereal solution dried over potassium carbonate, and evaporated, when p-*acetylaminophenylmethylhydrazine*,

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe{\cdot}NH_2,$$

remained as a dark oil.

This oil was now added to excess of *cyclo*hexanone, and the resulting hydrazone boiled with glacial acetic acid (10 grams), when the formation of the indole ring proceeded smoothly, and, on the addition of water, 6-*acetylamino*-9-*methyltetrahydrocarbazole* was precipitated. After crystallisation from acetic acid, this melted at 238° (Found : N = 11·5. $C_{15}H_{18}ON_2$ requires N = 11·6 per cent.) and was shown to be identical with the substance of this composition obtained from the product of the nitration of 9-methyltetrahydrocarbazole (p. 1835) by careful comparison and by the fact that the mixture of the two preparations melted at 238°.

5(?)-*Nitrotetrahydrocarbazole.*

Although tetrahydrocarbazole and 9-methyltetrahydrocarbazole, on nitration under the conditions given on pp. 1832 and 1834, give almost quantitative yields of the corresponding nitro-derivatives in which the nitro-group occupies the 6-position, 9-acetyltetrahydrocarbazole behaves quite differently. When nitration was attempted in sulphuric acid solution with potassium nitrate, an unsatisfactory product was obtained, from which nothing definite could be isolated by recrystallisation from the usual solvents.

It was, however, ultimately discovered that nitration may be satisfactorily carried out in glacial acetic acid solution under the following conditions. 9-Acetyltetrahydrocarbazole (3·6 grams) was dissolved in glacial acetic acid (50 c.c.) and then nitric acid (1·7 grams of *d* 1·4) diluted with a little glacial acetic acid gradually added at room temperature. The mixture was allowed to remain over-night, when long, pale yellow prisms separated which were collected and recrystallised from glacial acetic acid (Found : N = 10·7. $C_{14}H_{14}O_3N_2$ requires N = 10·8 per cent.).

5-*Nitro*-9-*acetyltetrahydrocarbazole* melts at 174° and is readily hydrolysed when it is warmed with a solution of sodium hydroxide in 50 per cent. aqueous alcohol. On the addition of water, a yellow, crystalline substance separates which may be crystallised either from alcohol or chloroform, from which it separates in long prisms (Found : C = 66·6 ; H = 5·6 ; N = 12·9. $C_{12}H_{12}O_2N_2$ requires C = 66·6 ; H = 5·5 ; N = 13·0 per cent.).

5-*Nitrotetrahydrocarbazole* melts at 172°, or at about the same temperature as the 6-nitro-derivative, and as it was at first thought that these two substances might be identical, a mixed melting-point determination was made, when the mixture began to melt at 125° and was completely melted at 151°.

7(?)-*Nitrotetrahydrocarbazole* and 8-*Chloro*-5-*nitrotetrahydrocarbazole* (X).

It has already been pointed out (p. 1828) that the action of *m*-nitrophenylhydrazine on *cyclo*hexanone might theoretically lead to the formation of 7-nitro- or 5-nitro-tetrahydrocarbazole or a mixture of both, and the following experiment was made with the object of ascertaining whether the product is actually a single substance or a mixture of isomerides. *cyclo*Hexanone-*m*-nitrophenylhydrazone (5·4 grams) was mixed with sulphuric acid (10 c.c.) and water (50 c.c.), in which it dissolved, but, on boiling, a brick-red, crystalline precipitate separated which was collected, washed with water, and dried. The yield of this substance was 82 per cent. of that theoretically possible, the loss being due to the hydrolysis of a little of the hydrazone into *m*-nitrophenylhydrazine and *cyclo*hexanone. In this condition, the substance melted at 154°, and this was not altered by recrystallisation from methyl alcohol, from which the substance separated in clusters of prisms and was obviously homogeneous. Although carefully searched for, no trace of any isomeride of this 7-*nitrotetrahydrocarbazole* could be detected.

8-*Chloro*-5-*nitrotetrahydrocarbazole* (compare p. 1829).—The preparation of this interesting substance was carried out under the following conditions. 2-Chloro-5-nitroaniline was prepared from *o*-chloroaniline by nitration in concentrated sulphuric acid solution, under the conditions recommended by Chattaway, Orton, and Evans (*Ber.*, 1900, **33**, 3062). This substance (6 grams) was added to concentrated hydrochloric acid (50 c.c.) and diazotised below 0° by the addition of sodium nitrite (2·5 grams) dissolved in a little water. A solution of stannous chloride (15·5 grams) in concentrated hydrochloric acid (20 c.c.) was then added, and the precipitate collected, washed with a little water, dissolved in much hot water, and the tin removed by means of hydrogen sulphide. The free 2-*chloro*-5-*nitrophenylhydrazine* was obtained from the filtrate by the addition of sodium acetate and was recrystallised from alcohol, from which it separated in long, orange needles melting at 160° (Found : N = 22·5. $C_6H_6O_2N_3Cl$ requires N = 22·4 per cent.).

*cyclo*Hexanone (1·3 grams) and 2-chloro-5-nitrophenylhydrazine (2 grams) were mixed together in boiling alcoholic solution, when, on cooling, cyclo*hexanone*-2-*chloro*-5-*nitrophenylhydrazone* separated in bright yellow prisms melting at 78° (Found: N = 15·7. $C_{12}H_{14}O_2N_3Cl$ requires N = 15·7 per cent.). The influence on the colour due to the introduction of the chlorine atom is very marked, since *cyclo*hexanone-*m*-nitrophenylhydrazone is bright red.

The hydrazone (2 grams) was now heated with sulphuric acid (4 c.c.) and water (20 c.c.), when 8-*chloro*-5-*nitrotetrahydrocarbazole* separated as a reddish-brown solid, which was purified by recrystallisation from alcohol, from which it separated in clusters of orange prisms melting at 214° (Found: N = 11·3. $C_{12}H_{11}O_2N_2Cl$ requires N = 11·2 per cent.).

Oxidation of Tetrahydrocarbazole and of 9-*Methyltetrahydrocarbazole.*

The interest attaching to the oxidation of hydrocarbazole derivatives is discussed in the introduction (p. 1830), and one of the objects we had in view was the discovery of a process which would be applicable, not only to the hydrocarbazoles themselves, but also to the chloro-, nitro-, and other derivatives. In the first experiments, the oxidation of tetrahydrocarbazole, suspended in dilute sulphuric acid at room temperature, with the theoretical quantity of permanganate was investigated. Oxidation took place very readily with almost immediate disappearance of the pink colour, but no carbazole could be isolated from the product. A similar negative result was obtained when tetrahydrocarbazole, without solution in dilute sulphuric acid, was oxidised with aqueous permanganate at about 80°. Subsequent experiments seemed to indicate that mercuric acetate may prove to be a useful reagent in such oxidations, as the following examples show.

Oxidation of Tetrahydrocarbazole to Carbazole.—This change takes place under the following conditions. Tetrahydrocarbazole (5 grams) is dissolved in glacial acetic acid (25 c.c.) at 85° and the solution added to the theoretical quantity of mercuric oxide (25·5 grams), dissolved in glacial acetic acid (25 c.c.), also at 85°. The mixture is heated on the steam-bath for a few minutes, allowed to cool, the mercurous acetate removed by filtration, and the filtrate diluted with water, when a yellow mercury compound of unknown composition separates. This was collected with the aid of the pump, washed with dilute nitric acid, and dried on porous porcelain. Hydrogen sulphide was now bubbled through this mercury derivative suspended in hot glacial acetic acid (50 per cent.), and the whole filtered hot, when, on dilution with water, the filtrate gave a small quantity of a solid which, after crystallisation from toluene, proved to be *carbazole*, but the yield was small.

Oxidation of 9-*Methyltetrahydrocarbazole to* 9-*Methylcarbazole.*

In this experiment, the oxidation with mercuric acetate was carried out under the conditions stated in the case of the oxidation of tetrahydrocarbazole and on diluting the filtrate from the mercurous acetate with water a sticky mass separated. This was extracted with chloroform, the solution dried over calcium chloride, the chloroform removed, and the residue distilled under 23 mm.

pressure, when metallic mercury and a colourless oil collected in the receiver. The oil soon solidified and, after crystallisation from alcohol, melted at 85—86° and proved to be 9-*methylcarbazole*, as a comparison of the properties and a mixed melting-point determination demonstrated. The yield was better than in the tetrahydrocarbazole experiment, and amounted to at least 20 per cent. of the theoretical.

Lastly, an experiment was made on the action of mercuric acetate on 6-nitrotetrahydrocarbazole, and in this case also mercurous acetate was formed, and water precipitated from the acetic acid filtrate a mercury derivative, the investigation of which is in progress.

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CCX.—*Some Properties of Fused Sodium Hydroxide.*

By THOMAS WALLACE and ALEXANDER FLECK.

THE amount of information available concerning fused sodium hydroxide is very small considering the enormous quantities which are produced and used every day in the chemical industry.

Certainly for one period in its production, and often continuously in its use sodium hydroxide is in the fused condition, and as such possesses many characteristic chemical properties, some of which are quite distinct from the properties of sodium hydroxide in solution.

This paper is a collection of some results obtained in the course of everyday working and experimenting with the fused material. It is divided into three sections.

Section A.—Estimation of moisture contained in sodium hydroxide.

Section B.—Action between sodium hydroxide and metals when heated in air.

Section C.—Action between metals and mixtures of sodium hydroxide and sodium peroxide.

A.—Estimation of the Moisture contained in Sodium Hydroxide.

The fact that sodium hydroxide, even when fused, contains moisture is quite well known, and various methods are available for removing it. Among these are

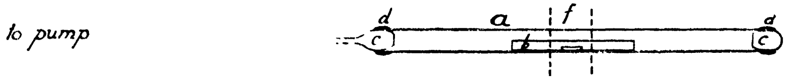
(1) The addition of sodium.

(2) Prolonged heating at 700° (Neuman and Bergve, *Zeitsch. Elektrochem.*, 1915, **21**, 143).

(3) Electrolytic decomposition.

None of these methods is easily applicable for a quantitative estimation. The suggestion of a suitable method came from some observations made when sodium hydroxide was being fused in a vacuum. An iron boat containing this material was placed in a horizontal glass tube connected with a mercury pump. The apparatus was evacuated and the sodium hydroxide slowly fused. As soon as the hydroxide melted, an extraordinarily vigorous bubbling and spitting took place. So much sodium hydroxide was thrown from the boat that the glass tube became quite opaque. This continued for some time, and then the alkali which was left in the boat became quiet, and it was seen that in the cooler portions of the tube moisture had condensed. By weighing the sodium hydroxide used and by absorbing the water in a weighed phosphoric oxide tube, the percentage of moisture could easily be obtained. This method with some modifications was used and the arrangement is shown in Fig. 1. A silica tube was used to minimise the risk of cracking. A metal tube was introduced in order to protect the silica, and the rounded glass plug with which the tube was sealed enabled a view of the boat to be obtained. The sodium hydroxide used, which had been fused for some weeks before being poured into the boat, was weighed with all possible speed. By handling the hydroxide quickly while it was warm, it could be got into the tube without taking any appreciable quantity of moisture from the air. When the boat had been placed in the tube and the apparatus evacuated, the tube was gradually heated to approximately 500° and this temperature was maintained for about an hour. Long before this time had elapsed all ebullition had ceased. After the apparatus had cooled, the phosphoric oxide tube was detached and weighed. It was found that the amount of moisture varied in different samples of sodium hydroxide. The lowest value observed was 0·9, the highest was 1·2, whilst the average value was 1·1 per cent.

FIG. 1.



(a) Silica tube. (b) Metal tube and boat. (c) Glass plugs. (d) Airtight sealing-wax joints. (e) Phosphoric oxide tube with pressure-tubing joints (c_1e_1). *(f) Portion of tube heated.*

It is interesting to note that if white, crystalline sodium hydroxide is put into the boat at the beginning, it will still be white at the end of the experiment. Had the fusion at 500° taken place in an iron boat in air, the sodium hydroxide would have become distinctly green. It was further observed that when green sodium hydroxide has been put into the boat initially, the hydroxide which remains in the boat at the end of the experiment has become pure white. These observations indicate:

(*a*) That air (or oxygen) is necessary to effect any solvent action between iron and sodium hydroxide at temperatures up to 500°.

(*b*) That in a vacuum, iron is capable of acting as a reducing agent in fused sodium hydroxide in the same way as sulphur, sodium, etc.

B.—Reaction between Sodium Hydroxide and Metals when Heated in Air.

Analysis of sodium hydroxide, even of the white, finished product, always reveals the presence of metallic impurities, usually oxides of iron, aluminium, nickel, manganese, calcium, and magnesium.

Sodium hydroxide fused in an iron vessel is invariably coloured, due to these metallic impurities (except immediately after treatment with some reducing agent, usually sulphur). The colour of the sodium hydroxide varies with the temperature and the relative proportion of metals dissolved. For example, if iron is predominant, then the sodium hydroxide has a green colour up to about 450—500°. At higher temperatures, it becomes blackish-yellow. If copper is predominant, the sodium hydroxide is coloured an intense blue, and so on.

It is interesting to note, in passing, that the amount of metals in solution is always very small, and that a very small percentage of metallic impurity produces a very strong coloration in the sodium hydroxide.

We have had occasion to examine many samples of commercial sodium hydroxide, which were in most cases very pure so far as other sodium salts are concerned, and we have never found the total percentage of metallic oxides to be more than 0·05 per cent. The bulk of this is usually iron and manganese, yet these small quantities are sufficient to colour the sodium hydroxide very deeply. In order to obtain a more complete knowledge of the behaviour of fused sodium hydroxide with metals, we conducted the several series of experiments given below.

1. *Action of Fused Sodium Hydroxide on Iron at Various Temperatures.*

Two sets of experiments were performed:

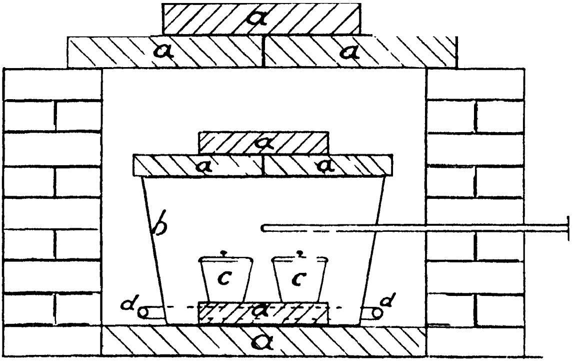
(*a*) With spun iron laboratory crucibles.

(*b*) With cast crucibles made from the iron used in the manufacture of ordinary melting pots for sodium hydroxide.

The sodium hydroxide used was of the best quality, never containing more than 1 per cent. of total impurity, of which the greatest part was sodium carbonate. The hydroxide was in the form of large, glistening crystals taken from the middle of a large mass, and small pieces of these were placed in the crucible.

The apparatus used is shown in Fig. 2, and with these arrangements it was possible to keep the temperature fairly constant to within 10°.

FIG. 2.



(*a*) *Firebricks.* (*b*) *Iron pot.* (*c*) *Iron crucibles.* (*d*) *Gas ring.* (*p*) *Pyrometer.*

The *modus operandi* was the same throughout the experiments. Two crucibles were placed in the furnace together and were used, when possible, throughout the series. Before each experiment, the insides of the crucibles were cleaned and burnished. Fifty grams of solid sodium hydroxide were introduced, and the crucibles were covered by loose lids, placed in the furnace, and kept at the required temperature for four hours. By heating the furnace to the required temperature before the crucibles were put in, a steady condition could be obtained within an hour.

At the end of four hours the crucibles were removed and the contents poured into nickel moulds. Each crucible was then thoroughly washed out and the washings were added to the solution of the main quantity of the sodium hydroxide. The total iron in the resulting liquid was estimated. Wherever possible, the amount

Observations made with Sodium Hydroxide and Laboratory Crucibles.

Temp.	No. of expts.	Frequence.	Colour of fused sodium hydroxide.	Condition.	Cooling phenomena.	Suspended matter.	Residue.	Iron in solution per cent.	Grams of iron removed from the crucible.
350°	9	8	Colourless.	Very turbid.	—	Red iron oxide.	None.	—	0·4
		1	,,	Crystal clear.	—	None.	,,	—	—
400	8	6	,,	Very turbid.	—	Red iron oxide.	,,	—	0·425
		2	Pale green.	,, ,,	—	,, ,, ,,	,,	—	0·425
450	8	8	Green.	Quite clear.	—	None.	Red iron oxide.	0·02–0·04	0·2–0·3
500	6	4	Almost colourless.	Clear.	Became turbid owing to the formation of a yellow ppte. as the hydroxide cooled.	,,	Very small amount of red oxide.	0·014–0·024	0·2–0·3
		2	Bright green.	,,	No ppte.	,,	,,	0·018–0·028	0·2–0·3
550	8	3	Almost colourless.	,,	Became turbid owing to the formation of a yellow ppte. as the hydroxide cooled.	Small yellow crystals resembling lead iodide crystallised from water.	,,	0·02	0·4–0·48
		5	Dark greenish-brown.	Almost opaque.	No ppte. seen.	None.	,,	0·048	0·09
600	6	5	Dark yellowish-green.	,, ,,	,, ,, ,,	Large quantity of crystals.	None.	0·068	0·3
		1	Dark brown.	,, ,,	,, ,, ,,	Very few crystals.	,,	0·068	0·13
650	1	1	Dark yellowish-green.	Opaque.	,, ,, ,,	Large quantity of crystals.	Red iron oxide.		

Note.—One experiment was performed in which a crucible containing sodium hydroxide was heated to 350°. After four hours the contents were examined and found to be red and turbid. The furnace was closed and allowed to cool very slowly. The final product was a solid mass of white sodium hydroxide in which all the red oxide had collected at the bottom.

of iron dissolved in the sodium hydroxide was estimated independently. The experiment was repeated three or four times at each particular temperature.

Table I gives the observations and data collected from the experiments conducted with laboratory crucibles. Particularly from 500° upwards, the action of sodium hydroxide and iron seems to be very complex, and at each of the temperatures taken we were met with absolutely different phenomena under what were, so far as we knew, the same conditions. The term " Frequence " in the table indicates for each particular temperature the number of times the phenomena described were met with. We are without any satisfactory explanation why this variation in the phenomena occurred.

Results with Cast Iron Crucibles.

The qualitative results were the same as those described in the case of spun crucibles, except in one particular. The sodium hydroxide obtained at 550°, when dissolved in water, gave a large quantity of purple precipitate, which yielded ferric hydroxide on keeping, or on the addition of water and was probably sodium ferrate. The total amount of iron removed was, however, much larger, and on the whole the tendency seemed to be for the quantity to rise with the temperature.

As in the previous experiments, the formation of the scintillating crystals was associated with a considerable rise in the total quantity of iron removed. The iron in solution was estimated and the quantity found to be of the same order as that estimated in the sodium hydroxide used with the other crucibles.

In generalising the results of these observations it should be clearly understood that they might be different if a period of heating other than four hours had been fixed upon. Practical experience, however, has shown that, in these experiments, the quantities of iron dissolved in the sodium hydroxide are of the same order as those contained in hydroxide which has been fused in iron pots for several weeks.

The quantitative results obtained with cast iron crucibles and those given in the table, are shown graphically in Fig. 3.

The important conclusions to be drawn from the table and the curves are as follows :

1. At temperatures up to and including 400° the ferric oxide formed by the action of sodium hydroxide and iron remains in suspension for at least several hours and practically no iron is dissolved.

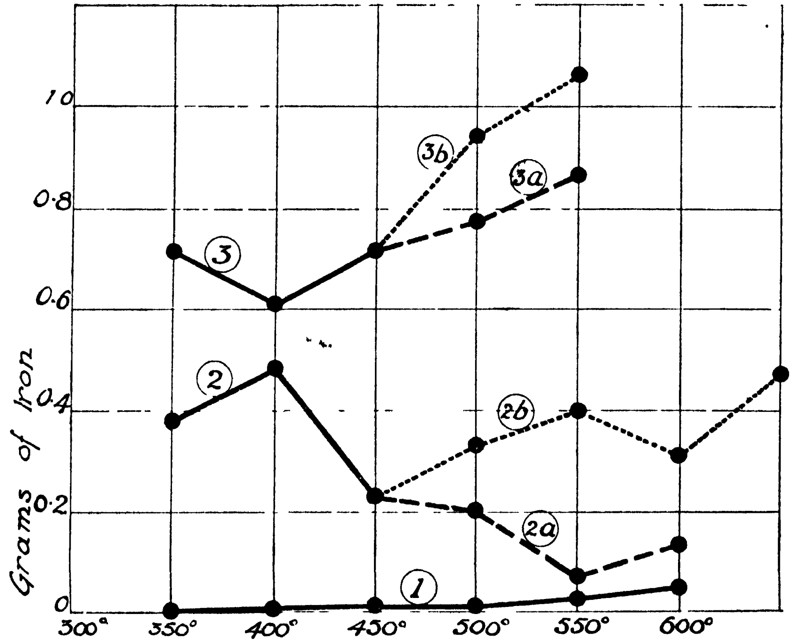
2. Between 400° and 500° the amount of iron removed is much

smaller. The red oxide formed settles to the bottom very quickly, except for a small amount which dissolves in the sodium hydroxide.

3. Between 500° and 550°, a soluble substance is formed which settles out as a yellow precipitate when the sodium hydroxide cools. This does not always occur.

4. At 550° and above, a yellow, crystalline substance is formed which is insoluble in sodium hydroxide at temperatures up to 650°.

FIG. 3.



Laboratory iron crucibles.—(1) *Quantity of iron dissolved.* (2) *Quantity of iron removed* (*a*) *when yellow precipitate and crystals are not formed ;* (*b*) *when yellow precipitate and crystals are formed.*

Cast iron crucibles.—(3) *Quantity of iron removed* (*a*) *when yellow precipitate is not formed ;* (*b*) *when yellow precipitate is formed.*

5. The graphs of the quantitative data show clearly that

(*a*) The amount of iron dissolved is very small compared with the amount removed.

(*b*) The amount dissolved increases with the temperature.

(*c*) With laboratory iron crucibles the amount removed falls rapidly from 400° to 600°, except when yellow crystals are formed. In these cases the amount is greatly increased.

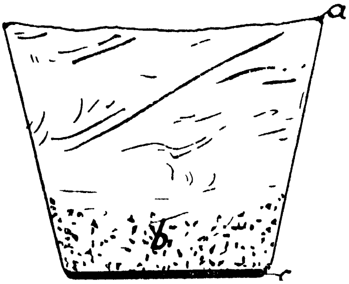
(*d*) With cast iron crucibles the tendency is for the amount removed to increase steadily with rise of temperature.

Isolation of the Crystalline Substance observed at 550° and above.

By the methods described above, it was impossible to isolate any of the crystals, as they were spread through the mass of the solid sodium hydroxide obtained in the mould, and treatment with water always gave a precipitate of ferric hydroxide, from which the crystals could not easily be separated. A new method had to be adopted.

The crucibles were treated exactly as before, the sodium hydroxide was introduced, and the crucibles were heated to 500—600° and left for four to eight hours. The gas was then turned off, the crucibles left in the furnace to cool slowly, and, when cold, the solid block of sodium hydroxide was tapped out of the crucible. The first result of this method was to reveal the presence of some dark red crystals which had not been seen before. The solid block of hydroxide was split vertically and gave a section sketched in Fig. 4. It will be observed that the red oxide and the yellow crystals had settled out very conveniently for purposes of separation, and that the dark red crystals were found at the point where air, iron, and sodium hydroxide meet.

FIG. 4.



(*a*) *Red crystals.* (*b*) *Yellow crystals.* (*c*) *Red iron oxide.*

The bottom of the block was split off and a piece of sodium hydroxide was thus obtained containing all the yellow crystals with a compact layer of red oxide on the bottom. This was completely scraped off with a knife, and the sodium hydroxide dissolved in water. A solution was obtained, with the yellow crystals and a small amount of the red oxide in suspension. The final separation was accomplished by spinning the solution round and then holding the beaker still. The red oxide rapidly settled out in a little heap on the bottom while the crystals were still carried round with the liquid. The latter was rapidly decanted off and carried the major portion of the crystals with it, while the red oxide was left in the beaker.

A sample of the dark red crystals was easily obtained by breaking off the sodium hydroxide at the edges, which was quite free from the red oxide, and dissolving it. Being at the edge, the crystals could be removed with only a very small amount of sodium hydroxide.

In this way a fairly large quantity of the yellow crystals was obtained, and a small quantity of the darker crystals. The yellow crystals consist of iron, sodium, and oxygen, and their chemical properties are identical with those of the red crystals described on p. 1854. The presence of sodium was first indicated in an attempt to estimate the oxygen by reduction in a stream of hydrogen. Very varying results were obtained, and in all cases the boat (both platinum and silica were used) showed signs of having been acted on. This disproved the suggestion that the yellow crystals might be crystalline oxides of iron.

The analysis of the crystals proved very unsatisfactory. The estimation of the iron was effected without difficulty, but even here the results obtained were never within the limits of experimental error, although they were always fairly close to one another. The estimation of the sodium was completely unsatisfactory, the difficulty being to obtain a suitable method. This difficulty was overcome later and the method finally employed to estimate the sodium will be fully dealt with in section *C*.

Several analyses were performed (Found : Fe = 56·3; Na = 14·8; O = 28·9 per cent.), but the figures correspond with no simple formula ($Na_3Fe_5O_9$ is the simplest), and cannot be regarded as giving more than an indication of the composition of the crystals.

Owing to the trial of one method after another, our sample was almost exhausted. Our old crucibles were worn out, and we had to wait many months before new ones could be obtained (1917—18). When we did get them, we were totally unsuccessful in our attempts to prepare anything like reasonable quantities of the crystals. The reason for this is not evident. The matter was allowed to rest there until another series of experiments was performed, which is described in section *C*.

2. *Action of Fused Sodium Hydroxide on Nickel at Various Temperatures.*

Ordinary laboratory nickel crucibles were used, and the gas-fired furnace was replaced by an electrically-heated muffle. In each experiment two crucibles containing 150 grams of sodium hydroxide

TABLE II.

Observations made with Sodium Hydroxide and Nickel.

Temp.	No. of expts.	Frequence.	Colour of fused sodium hydroxide.	Condition.	Cooling phenomena.	Suspended matter and residue.	Nickel in the solution per cent.
Series 1 with new crucibles.							
360°	8	4	Very pale green.	Clear.	Set to white solid with purple tint.	None.	0·01–0·02
		4	Pale green.	Clear, with slight scum.	Black ppte. on cooling.	,,	0·01–0·02
400	10	2	Colourless.	Clear.	No ppte.; set to pure white solid.	,,	Trace.
		5	Pale green.	Clear, with slight scum.	No ppte.; set to yellow solid.	,,	0·008
		1	Very pale green.	Clear.	—	Small quantity of small, silvery crystals floating in the sodium hydroxide.	0·014
		2	Greenish-yellow.	Clear, with scum.	Black ppte. on cooling.	—	0·02
Series 2 with same crucibles as before.							
350	4	4	Green.	Clear, with scum.	Black ppte. on cooling.	—	0·01–0·03
375	6	6	,,	,, ,, ,,	,, ,, ,, ,,	—	0·01–0·03
400	4	4	,,	More scum.	,, ,, ,, ,,	—	0·01–0·02
450	4	4	,,	No scum.	Much less ppte.	—	0·01–0·02
500	6	6	,,	,, ,,	Very little ppte.	—	0·005–0·015

and fitted with fairly tight nickel lids were used. The nickel in the hydroxide was estimated by dissolving the product in hydrochloric acid and precipitating the nickel by dimethylglyoxime in the usual way. The phenomena observed were very inconsistent. Owing to this, one series of experiments was abandoned altogether, and another undertaken with the intention of raising the temperature by steps of 20° rather than 50°.

It is very difficult to sum up the reaction of nickel and sodium hydroxide. The most feasible line of explanation is that the inner surface of the crucible is oxidised in some way which is not very clear. It is well known that nickel oxide is only very slightly soluble in sodium hydroxide, and it would consequently form a protective covering. This would account for the small quantities of nickel found in the alkali and for the absence of anything comparable with the red oxide obtained with iron crucibles. The production of the silvery crystals observed in one isolated case will be fully dealt with in section *C*. In some cases, similar to what we once or twice obtained with iron crucibles, there seemed to be no action whatever. The explanation of such cases, in which the inside surface of the crucibles remained quite bright and clean, would seem to be one where the metal was in the passive state. It should be noted, however, that these negative results were not obtained after the crucibles had been used for a while.

3. *Action with Copper at Various Temperatures.*

A similar series of experiments to those performed with nickel was undertaken with two crucibles beaten out of $\frac{1}{8}$-inch sheet.

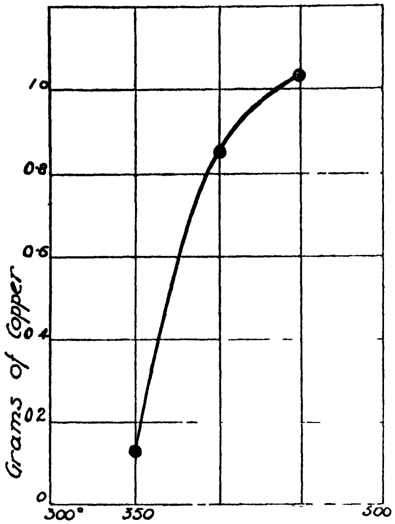
With copper there seemed to be a very complex action, judging by the various phenomena which were observed. In contradistinction to iron, the phenomena were almost the same for various temperatures, but they became intensified as the temperature rose.

The following phenomena were observed at 350°, and in a greater degree at higher temperatures.

The fused sodium hydroxide was clear and intensely blue and contained a number of shiny scales floating in it. On pouring the melt into a cold mould, the first sodium hydroxide to touch the mould instantly became intensely yellow, whilst the rest of the hydroxide, cooling comparatively slowly, deposited a red substance. The final solid was dark red, with a bright yellow surface where it had been in contact with the mould. This yellow effect was without doubt due to the sudden cooling of the sodium hydroxide.

Several interesting phenomena were observed during the analysis of the sodium hydroxide. When the alkali was put into water, a vivid yellow substance was precipitated, and this was followed by the precipitation of a bright red powder. After keeping, the whole precipitate turned red. The solution itself was of a blue colour, which deepened on keeping. The copper was estimated by precipitation with hydrogen sulphide in the usual way after the addition of hydrochloric acid. This precipitation was somewhat curious. The hydrochloric acid solution was yellowish-green and gave a precipitate only very slowly with hydrogen sulphide, in fact, a few minutes elapsed before the gas produced any precipitate at all. When, however, the acid solution was first boiled with a little sodium hydrogen sulphite, the hydrogen sulphide immediately gave a precipitate.

Fig. 5.



As the temperature rose, the colour of the fused sodium hydroxide deepened, and at 450° it had a distinctly brown tint. The number of shiny scales in the hydroxide increased considerably, and this probably accounts for the big increase in the percentage of copper in the alkali. No attempt was made to isolate any of the crystals, as they were invariably mixed with a red precipitate which accompanied the solution of the sodium hydroxide. They were also acted on by water, and after remaining for a short while were decomposed.

At 500° an interesting change was observed. The sodium hydroxide was very dark brown, and a large quantity of crystalline matter was found in the bottom of the crucible. The crystals were long and narrow, and quite different in shape and appearance from the scales observed at lower temperatures. At 550° still more of these crystals were formed. It was possible to pour off the sodium hydroxide and leave the crystals in the crucibles. They were removed, rapidly washed, and dried. In this way an impure sample was obtained, from which some large crystals were picked out.

The sodium hydroxide obtained at these high temperatures is very pretty when cooling in the mould, and finally gives a crystalline solid totally different in crystalline character from ordinary sodium hydroxide.

At the lower temperatures the total percentage of copper in the

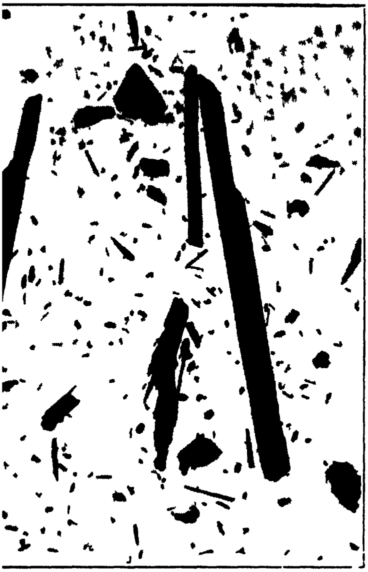


PLATE 1 × 30

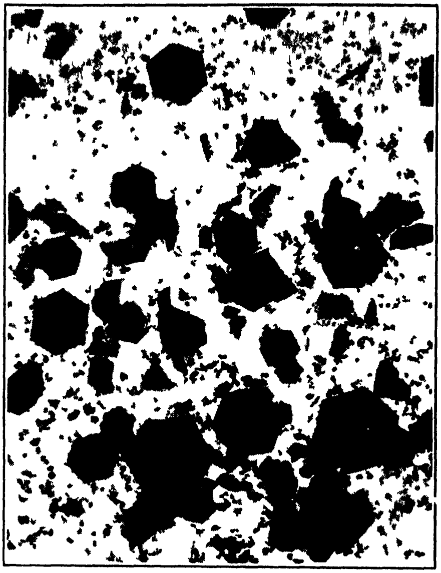


PLATE 2 × 30

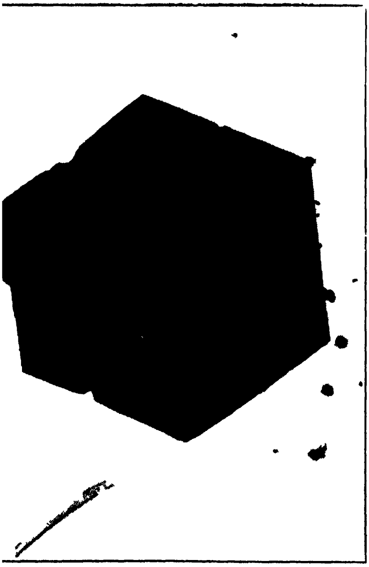


PLATE 3 × 30.

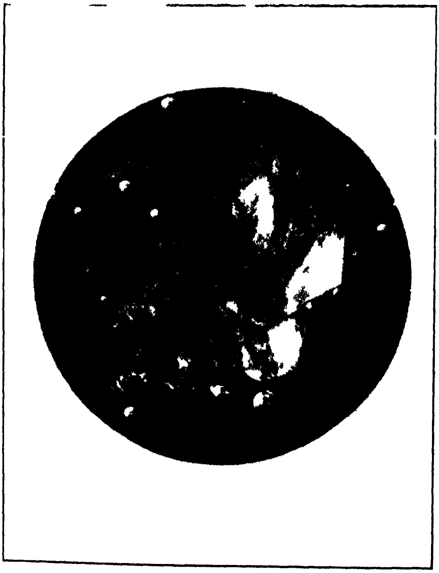


PLATE 4 × 30.
Reflected light.

[*To face p.* 1851, *Trans*

sodium hydroxide was 0·067 at 350°, 0·440 at 400°, and 0·536 at 450°. Since the scales were always found in suspension, the above figures do not represent the exact amount of copper dissolved in the sodium hydroxide, but they give some idea of the relative amounts of copper dissolved from the crucible. The data, shown graphically in Fig. 5, refer to 200 grams of sodium hydroxide heated for four hours.

As there was not sufficient picked material, the analysis of the crystals was made on the impure sample. It consisted of a mixture of very small crystals and a little amorphous copper oxide. The sample was dissolved in hydrochloric acid, the copper precipitated in the usual way, the filtrate evaporated to dryness, and the residue dissolved and titrated with standard silver nitrate. The precipitate of copper sulphide was redissolved, and the copper estimated electrolytically.

The following are the analytical data:

Weight of sample	1·1131 grams.
„ of copper found	0·8716 gram.
„ of sodium in the filtrate	0·00591 „

It is reasonable to assume that such a small amount of sodium must be present as an impurity—probably due to incomplete washing, in which case it would be present as sodium carbonate. The weight of carbonate present would be 0·0131 gram. On this assumption, the actual weight of the crystals was 1·1131 — 0·0131 = 1·100 grams. The percentage of copper in the crystals was therefore 79·2. This gives a final proportion of Cu : O = 1·247 : 1·3 = 1 : 1·04. From this it would seem that the crystals are a crystalline oxide of copper of the empirical formula CuO.

When examined with transmitted light, the crystals are quite opaque. From the photograph (Plate 1, magnification 30 diameters) it is seen that they are long, needle-shaped crystals which have, in unbroken specimens, truncated ends.

Conclusions.

(1) Compared with iron and nickel, copper can be said to be readily attacked and dissolved by fused sodium hydroxide.

(2) The actual amounts are still quite small—the highest being in the sodium hydroxide heated at 450°, which contains approximately 0·8 per cent. of copper, but it will be seen that the actual quantities are much greater than in the case of either iron or nickel. Since copper is much more easily oxidised than the other two metals, this supports the view that all these reactions of fused sodium hydroxide with metals commence with the oxidation of the metal.

(3) Crystals are obtained in the sodium hydroxide at all tem-

peratures. At 350° to 500°, shiny scales are observed in the hydroxide. Above 500°, the scales disappear and long, thin crystals are seen floating in the liquid.

(4) These long crystals are readily soluble in acids, are decomposed by water after a while, and are quite different in character from the crystals obtained with iron and nickel. Their empirical formula is CuO.

C.—Action of Mixtures of Sodium Hydroxide and Sodium Peroxide on Metals.

1. *Action with Iron.*

In the previous section of this paper, reference was made to two kinds of crystals (yellow and red) produced by the action of sodium hydroxide on iron at temperatures above 550°. The second attempt to prepare any quantity of these, was, for some unknown reason, unsuccessful. It was thought that these crystals were the product of some oxidation process, and the lack of success in their preparation seemed to indicate the necessity for some stronger oxidising agent. To achieve this, it was decided to add sodium peroxide. A preliminary experiment was carried out in one of the crucibles used previously. A mixture of sodium hydroxide and 5 per cent. of sodium peroxide was heated in an iron crucible at 500 to 550° for four to eight hours. The crucible and contents were then allowed to cool very slowly in the furnace. When the sodium hydroxide was quite cold, it was found that a large quantity of red crystals had been formed. The crystals were found adhering to the crucible and the surface of the sodium hydroxide, and they were much larger and better formed than any obtained previously. The hydroxide was broken up, but no sign of the yellow crystals was seen. As the addition of sodium peroxide seemed to give a very promising result, a complete series of experiments was carried out at various temperatures. Unless otherwise stated, the sodium hydroxide in the following experiments always contained 5 per cent. of sodium peroxide.

Results obtained.

Temp.	Description of the sodium hydroxide.	Particulars of crystals observed.	Percentage of iron in the solution.
350°	Greenish-blue.	Quantity of very small crystals.	0·024
	Free from suspended matter.	Mixed with the red oxide.	
400	Free from suspended matter.	Mixed with the red oxide.	0·025
450	Very black; gave a yellow pptc. on cooling.	Large quantity of red crystals in suspension.	0·11

Results obtained at 500—550°.

On one occasion a clear, dark green sodium hydroxide was formed which gave no yellow precipitate on cooling and in which there were no crystals of any kind. It contained 0·029 per cent. of iron in solution. This was quite evidently one of the exceptional cases which were met with every now and then.

The general results of heating sodium hydroxide with 5 per cent. of sodium peroxide in an iron crucible to 550° and leaving to cool slowly after about five hours' heating, were as follows:

(1) A large quantity of red crystals was formed.

(2) The sodium hydroxide was a dark, almost black, quite soft solid which dissolved in water very readily, usually with evolution of gas. The solution was deep purple, which rapidly became deep green, a large quantity of ferric oxide being precipitated. The green solution seemed permanent when very concentrated.

(3) When the sodium hydroxide was dissolved in a minimum quantity of water and the concentrated solution poured off after the insoluble matter had been allowed to settle, a mixture of substances was found in the sediment. In this, which was principally ferric oxide, there were a few red crystals and two substances different in appearance from anything we had seen previously. The separation of the latter substances was not attempted on any scale, but a few specimens were picked out and examined microscopically. Of the two new substances, one was in the form of long, narrow, blood-red crystals (almost opaque) with peculiar truncated ends, which were rapidly decomposed by water and deliquesced in the air. The other, of which there was a moderate quantity, consisted of small, flat pieces of rust-coloured matter. It was difficult to tell whether these were crystalline or not. They generally had a peculiar red sheen with reflected light.

An excellent sample of the red crystals was obtained by carefully cutting off the masses of crystals which had collected at the edge of the solid sodium hydroxide and dissolving in water. The crystals were so thick that they could be detached with very little adhering sodium hydroxide.

Results at Higher Temperatures.

Two iron crucibles containing sodium hydroxide with 5 per cent. and 10 per cent. of peroxide respectively were heated at 720° and allowed to cool very slowly in the furnace.

The hydroxide containing 5 per cent. of peroxide set to a green solid. On dissolving in water, a large quantity of the long, red crystals with truncated ends was observed along with a small quantity of red crystals.

The hydroxide with 10 per cent. of peroxide set to a dark purple solid, and red crystals had been deposited in considerable quantity on the sides of the crucible. A large quantity of the long crystals and a small quantity of the red variety were seen when the sodium hydroxide was dissolved. It is seen from this that the long crystals are the product of reactions carried out at the higher temperatures.

Results obtained with the Use of Pure Sodium Peroxide.

It was found that the employment of larger quantities of sodium peroxide than those used, resulted in the crucibles being attacked very vigorously. Ordinary laboratory crucibles were usually eaten right through. In addition to this, it was found that as the amount of peroxide used was increased, the amount of crystals of all kinds diminished until with large amounts, such as 50 per cent., no crystals were found at all.

A thick cast-iron crucible containing sodium peroxide only was heated at 500—550° for about four hours, and left to cool in the usual way. The final product was a mass of long, very dark crystals which dissolved in water very readily, yielding a deep purple solution which deposited ferric oxide and turned green on keeping. These crystals were probably pure sodium ferrate.

Properties of the Red Crystals formed at 500°.

1. When examined under the microscope, it was seen that the crystals tended to be very perfect hexagons. All the available evidence, microscopic as well as chemical, showed that the yellow crystals and the red crystals are both modifications of one substance. The crystals are transparent and of a reddish-brown colour, the intensity varying with the thickness of the crystal. They have a refractive index slightly greater than that of oil of cinnamon ($n = 1{\cdot}58$). Most of the crystals are lamellar and are really basal cleavage plates of hexagonal crystals which have a very perfect basal cleavage. With convergent light they readily give optical figures which show that the crystals are uniaxial and optically negative. A microphotograph (Plate 2, magnification 30 diameters) is given, in which the crystals, being red, appear quite black, and which shows the regular hexagon shape of the untouched crystals.

2. They are unacted upon by boiling water, boiling sodium hydroxide solution, and cold dilute mineral acids.

3. They are readily dissolved by hot concentrated acids.

4. They are stable up to at least 720° in fused sodium hydroxide.
5. They consist of sodium, iron, and oxygen. In view of this composition their stability is remarkable.

Analysis.

A known weight of the crystals was washed with water and the amount of Na_2O in the washings estimated.

The washed crystals were dissolved in hydrochloric acid, and the solution was carefully evaporated to dryness in either a platinum or porcelain dish. The residue was then gently heated until a constant weight was obtained, indicating that all the ferric chloride had been converted into oxide. The final residue was boiled with water, and the sodium chloride in the resulting liquor estimated by titration with silver nitrate. The sodium oxide estimated in the washings was assumed to be carbonate, and allowance was made for this in calculating the results. The solution of the crystals in acid was made up to 250 c.c. and 50 c.c. taken for each sodium estimation. The sodium figures for various estimations on the same solution agreed fairly well, showing that the method was satisfactory. The analysis of the crystals was never satisfactory.

The following are the average results of an analysis made immediately after the crystals were isolated: Fe = 52·2; Na = 14·55; O = 30·25 per cent.

Analyses made on a washed sample twelve months after its formation gave an iron content larger than the above by approximately 6 per cent.

It seems fairly definite that the crystals are composed of a mixture of oxides of sodium and iron, the latter probably functioning in an acidic capacity. The variations in the analyses are most likely due to the crystals themselves undergoing slow decomposition, which would of course introduce differences. This is shown by the fact that no matter how carefully the crystals are washed, if they be kept for any length of time and then rewashed, the washings will always contain a further quantity of sodium. No weight can therefore be put on the analysis for the purpose of obtaining a molecular formula, but it seems possible that immediately after the removal they have a composition represented by the formula $Na_2Fe_3O_6$.

2. *Action with Nickel.*

A series of experiments similar to those with iron crucibles were carried out with nickel. These experiments were made at the

TABLE III.

Results with Nickel and Sodium Hydroxide containing Sodium Peroxide.

Temp.	Sodium peroxide per cent.	Colour of fused sodium hydroxide.	Condition.	Cooling phenomena.	Suspended matter.	Percentage of nickel in the sodium hydroxide.
350°	5	Dark green.	Clear, with slight scum.	Black ppte. on cooling.	None.	0·0024
400	,,	Brown.	Clear.	Large black ppte. and vigorous bubbling on cooling.	Large quantity of silvery crystals.	0·0135
450	,,	,,	,,	,, ,, ,, ,,	,, ,, ,, ,,	0·0131
500	,,	,,	,,	Large black ppte., but no bubbling.	Larger quantity of crystals.	
720	,,	Allowed to cool slowly in the furnace. Grey solid.			Few crystals on the surface. None in the mass of the sodium hydroxide.	
	10	Allowed to cool slowly in the furnace. Shiny black mass of sodium hydroxide and silvery crystals, more like graphite than sodium hydroxide. Apart from the crystals, the hydroxide had crystallised in a kind of check pattern, totally different from anything seen before.				

same time as the second series of experiments with sodium hydroxide and nickel, the crucibles all being in the furnace together. The principal aim was to ascertain if the silvery crystals observed on one occasion in the first series would be produced in any quantity by the addition of sodium peroxide to the hydroxide.

From Table III it is seen that this object was accomplished, and from the mass of silvery crystals obtained at 720° a large sample was prepared.

These crystals were much more easily separated than the corresponding iron ones, as there was practically no precipitate when the sodium hydroxide dissolved in water, and nothing analogous to the red oxide. A little nickel oxide was present, but this was easily got rid of by swirling the solution and decanting the liquor containing the bulk of the crystals. There were no signs of any other crystalline substances.

Examination of the Crystals.

(1) When examined under the microscope with transmitted light, these crystals are quite opaque. They are, however, very similar in form to the crystals obtained with iron crucibles, that is, they crystallise in regular hexagons, as is shown from a single crystal on Plate 3. If, however, they are examined with reflected light, it is seen that the crystals are regularly etched. Frequently the etching is seen as parallel bands, very similar in appearance to the parallel twin bands of plagioclase. At times, however, more or less complete equilateral triangles are seen (Plate 4), which shows that the crystals have symmetry of the hexagonal system.

(2) The crystals are stable in fused sodium hydroxide up to 750° and are unacted on by water and cold dilute acids.

(3) They are readily dissolved by hot concentrated acids, and liberate chlorine from hydrochloric acid.

(4) They consist of nickel, sodium, and oxygen.

Analysis.

This analysis was again unsatisfactory, but an average analysis gives Ni = 53·6; Na = 8·4; O = 38·0 per cent.

The sodium was estimated in the manner described for the iron compound. The nickel chloride was very readily reduced to the oxide. The percentage obtained was the average of several results obtained on four lots of the solution, namely, 8·38, 8·7, 8·5, 8·46. The nickel was estimated by the glyoxime method, and the oxygen by difference. The average analysis indicates an empirical formula

TABLE IV.

Results with Copper and Sodium Hydroxide containing Sodium Peroxide.

Temp.	Sodium peroxide per cent.	Description of the sodium hydroxide.	Behaviour with water.	Crystals observed.	Percentage of copper in the solution.
350°	5	Dark brown and clear.	Dissolved readily with evolution of gas, giving clear, colourless solution.	None.	Trace.
400	,,	,, ,, ,, ,,	,, ,, ,,	,,	0·013
450	,,	,, ,, ,, ,,	Pale blue solution.	,,	0·08
500	,,	,, ,, ,, ,,	,, ,, ,,	Large quantity of brown, shiny scales similar to those obtained with sodium hydroxide alone at 350–500°.	
550	,,	,, ,, ,, ,,	,, ,, ,,	A few long crystals in suspension.	
350	10	Greyish solid with the "check" crystalline appearance previously noted.	Clear blue solution.	None.	0·05
400	,,	Black solid.			0·14
450	,,	"Check" crystalline appearance very pronounced.		A few crystals adhering to the crucible.	

of $Na_2Ni_5O_{13}$. It was found that the crystals were unstable over long periods of time and in this respect were similar to the iron crystals already described. When crystals which had been very thoroughly washed with water were kept for a period of, say, a week, sodium compounds were always found in the washings when they were rewashed. This will account for the unsatisfactory analysis.

3. *Action with Copper.*

A parallel series of experiments to those described with copper and sodium hydroxide was carried out in similar crucibles with sodium hydroxide and 5 per cent. of sodium peroxide. A few additional experiments with 10 per cent. of peroxide were performed. The results obtained (see Table IV) were quite unexpected, being the reverse of those obtained with iron and nickel. There, the action on the metal was much increased by the addition of peroxide, whilst with copper the action was considerably reduced.

Conclusion.

So far as the formation of crystalline substances and the removal of copper from the crucibles are concerned, the addition of the peroxide seemed to have a prohibiting effect, in marked contrast to that produced by peroxide with iron or nickel crucibles.

Summary.

The chemical properties of fused sodium hydroxide have been studied in three respects.

(1) *The Water Content.*

By fusing sodium hydroxide in a vacuum, it has been found that it has an average water content of 1·1 per cent. In connexion with these experiments, it is evident that the presence of oxygen is necessary before the fused hydroxide becomes coloured in its usual manner. In a vacuum, the iron of the containing vessel is able to act as a reducing agent on the small quantities of impurities in the hydroxide.

(2) *Action on iron, nickel, and copper in air.*

(*a*) These reactions have been studied between 350° and 600°.

(*b*) In no case is the amount of metal dissolved in the sodium hydroxide very high. The maximum amount, which was obtained with copper, was 0·73 per cent.

(*c*) Iron is less vigorously attacked than copper, and more vigorously than nickel.

(*d*) The formation of crystalline substances by the action of fused sodium hydroxide on each of these metals has been noted and their separation described.

(3) *Action of iron, nickel, and copper with sodium hydroxide containing* 5 *per cent. of sodium peroxide.*

(*a*) This action has been studied at temperatures ranging from 350° to 720°.

(*b*) The formation of crystalline substances previously noted is found to be facilitated in the case of iron and nickel at certain temperatures between 500° and 700°. The substances formed in the largest quantities have been described and analysed. In the case of copper, the formation of crystals is retarded.

(*c*) The reaction between sodium hydroxide, sodium peroxide, and iron or nickel is almost certain to have a parallel with similar metals such as cobalt, chromium, or manganese, and it is extremely probable that research with other metals on the lines indicated would reveal the presence of new crystalline substances, similar to those we have described.

We desire to express our thanks to the Directors of the Castner-Kellner Co., Ltd., for facilities granted at their Wallsend works, and also to Mr. L. Hawkes, M.Sc., for assistance in connexion with the crystallographic measurements.

[*Received, July* 15*th*, 1921.]

CCXI.—*Some Derivatives of Monothioethylene Glycol.*

By George Macdonald Bennett and Edith Muriel Whincop.

The preparation of monothioethylene glycol was recently described (this vol., p. 423) and we have now prepared a few crystalline derivatives of this interesting and reactive substance. As one of us is obliged to withdraw from the work, it seems best to publish the results which have so far been obtained.

Owing to the tendency of the mercaptan to become oxidised in alkaline solution, a Schotten-Baumann reaction led to the corresponding acylated disulphide. Mercaptans have been shown (Goldschmidt and Meissler, *Ber.*, 1890, **23**, 272) to react with phenylcarbimide in a manner analogous to the reaction with alcohols; with monothioethylene glycol, the molecule of which contains both a thiol and a hydroxyl group, phenylcarbimide reacted at once, addition taking place, as was perhaps to be expected, preferentially at the thiol group, and a substance was produced of the formula $C_6H_5{\cdot}NH{\cdot}CO{\cdot}S{\cdot}C_2H_4{\cdot}OH$.

It was hoped that the series of compounds $S(C_2H_4{\cdot}OH)_2$, $C_2H_4(S{\cdot}C_2H_4{\cdot}OH)_2$, $S(C_2H_4{\cdot}S{\cdot}C_2H_4{\cdot}OH)_2$, etc., might be extended by successive condensation of the corresponding halogen compounds with monothioethylene glycol. An examination of the higher members of this series, or of the unsaturated substances derived from them, which evidently approximate more and more closely in composition to diethylene disulphide, might throw light on the nature of the amorphous products of high molecular weight obtained from the interaction of ethylene dibromide and alkali sulphides by Crafts (*Annalen*, 1862, **124**, 110; 1863, **128**, 220), V. Meyer (*Ber.*, 1886, **19**, 3262) and Mansfield (*ibid.*, 1886, **19**, 697). The series was not, however, carried beyond the third member, for the dichloro-compound derived from this seems to be much more unstable than its lower homologues, and could not be isolated. Ethylene *bis*-β-chloroethyl sulphide,

$$CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl,$$

has the very reactive chlorine common with β-chloro-sulphides, and its physiological action is very noticeable. In marked contrast to this is the low reactivity of the halogen in the β-halogenated 2 : 4-dinitrophenyl ethyl sulphides.

EXPERIMENTAL.

β-*Hydroxyethyl phenylthiocarbamate*, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}S{\cdot}C_2H_4{\cdot}OH$, was produced when molecular proportions of phenylcarbimide and monothioethylene glycol were warmed together for a few seconds. It is a cream-coloured solid of m. p. 59—60°, which crystallises well from benzene or carbon tetrachloride (Found : N = 7·19; S = 16·0. $C_9H_{11}O_2NS$ requires N = 7·11; S = 16·25 per cent.). It is easily soluble in these solvents or in alcohol, but insoluble in light petroleum or water. It shows none of the reactions of a mercaptan, giving no mercury compound when its alcoholic solution is boiled with mercuric oxide, and having no reducing action on ferric chloride.

ββ′-*Di*-p-*nitrobenzoyloxydiethyl disulphide*,

$$(NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2)_2S_2,$$

was the main product when monothioethylene glycol was treated with *p*-nitrobenzoyl chloride in presence of aqueous sodium hydroxide. It crystallised in pale buff-coloured plates from butyl alcohol or methyl acetate, m. p. 145° (Found: N = 6·1; *M* = 353. $C_{18}H_{16}O_8N_2S_2$ requires N = 6·2 per cent.; *M* = 452). The product from the above reaction contained also a substance of lower melting point, which was continually oxidised during purification with production of the disulphide.

An *additive* compound, C_2H_6OS,C_2HOCl_3, was formed with evolution of heat when the mercaptan was mixed with chloral in benzene solution. It crystallised in colourless needles on addition of light petroleum, and melted rather indefinitely at 67—68°. The substance was very deliquescent and too unstable to purify (Found : Cl = 50·7, 51·2. $C_4H_7O_2Cl_3S$ requires Cl = 47·2 per cent.).

Ethylene bis-β-*Hydroxyethyl Sulphide*,
$HO{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.
—Ethylene dibromide (12 grams) was cautiously added to a solution prepared from sodium (3 grams) and the monothioglycol (10·5 grams) in rectified spirit (60 c.c.). The solution became neutral to litmus after boiling for fifteen minutes; the sodium bromide was removed by filtration and the filtrate evaporated. The crude product (obtained in quantitative yield) was purified by recrystallisation from methyl acetate or ethyl ether, from which it separated in colourless plates melting sharply at 64° (Found : C = 39·2; H = 7·67. $C_6H_{14}O_2S_2$ requires C = 39·5; H = 7·70 per cent.).

This substance is readily soluble in water, alcohol, or hot methyl acetate, less so in benzene or light petroleum. Its solution in alcohol (and that of the corresponding trisulphide described below) dissolves a considerable quantity of sodium chloride. It is stable to heat, distilling undecomposed at atmospheric pressure. Considerable difficulty was found in analysing it, an unusual length of combustion tube being necessary to ensure complete oxidation. A crystalline methiodide could not be obtained. When the substance was heated with boiling concentrated hydrochloric acid, it dissolved, and an oil separated which solidified in the cold. This was crystallised from light petroleum, but was apparently a mixture, its low chlorine content showing that any dichloro-compound produced had partly decomposed—probably with production of the corresponding unsaturated compound.

Ethylene bis-β-*Chloroethyl Sulphide*,
$CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl$.
—The pure dihydroxy-compound described above was dissolved in an excess of purified thionyl chloride, and when the reaction was complete, the excess of the reagent was removed by heating on the water-bath under diminished pressure. The residue crystallised on cooling, and the colourless crystals were drained on porous earthenware in a desiccator over potassium hydroxide (Found : Cl = 30·4. $C_6H_{12}Cl_2S_2$ requires Cl = 32·4 per cent.). The compound melts at 54°. The reactivity of the chlorine is similar to that found with ββ′-dichlorodiethyl mono- and di-sulphides (com-

pare this vol., p. 424), and although no exact comparison has been made, the substance appears to have a distinctly stronger vesicant action than ββ′-dichlorodiethyl sulphide. When attempts were made to recrystallise it from light petroleum, it became partly decomposed or hydrolysed (Found: Cl = 12·7 per cent.).

Sulphido-bis-β-*hydroxydiethyl Sulphide*, $S(CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_2$.—ββ′-Dichlorodiethyl sulphide (5·3 grams) was added to a solution prepared from a slight excess over the calculated weights of monothioethylene glycol and sodium in rectified spirit (20 c.c.), and the reaction was completed by heating on the water-bath for a few minutes until the alkalinity had disappeared. The solution, separated by filtration from the sodium chloride which had been precipitated, deposited a white solid on cooling. This was purified by crystallisation from hot acetone or methyl acetate, in which it was readily soluble, and was thus obtained as colourless plates, m. p. 91—92° (Found: C = 39·2; H = 7·35. $C_8H_{18}O_2S_3$ requires C = 39·6; H = 7·45 per cent.). This substance is less readily soluble in water or alcohol than the disulphide described above. It resembles the latter in its behaviour when heated with concentrated hydrochloric acid. When attempts were made to convert it into the corresponding dichloro-compound by the action of thionyl chloride, as with the dihydroxy-disulphide, a sudden evolution of gas occurred on raising the temperature, owing to decomposition, and no definite compound was isolated.

A *diacetyl* derivative was obtained by acetylation with acetic anhydride and sodium acetate as a white solid, m. p. 51° after crystallisation from light petroleum (Found: C = 44·2; H = 6·69. $C_{12}H_{22}O_4S_3$ requires C = 44·2; H = 6·76 per cent.).

Condensation of Monothioethylene Glycol with Chloro-2 : 4-dinitrobenzene.

When chloro-2 : 4-dinitrobenzene was treated with a solution of the sodium salt of the monothioglycol (1 equivalent) in rectified spirit, the desired sulphide was produced in almost the calculated yield, provided that the solutions were mixed cold and the temperature of the mixture was not allowed to rise rapidly. Otherwise a violent reaction occurred, the solution became almost black, and a chocolate-brown solid subsequently crystallised, having m. p. 143°, which did not contain sulphur and was probably an azoxy-compound. When the reaction proceeded smoothly, the sodium chloride quickly separated as the temperature was gradually raised, and the reaction was completed by heating the solution for a few minutes on the water-bath. The product was precipitated by pouring the solution into a large volume of water, and was recrystallised from benzene.

2 : 4-*Dinitrophenyl β-hydroxyethyl sulphide*,

$$C_6H_3(NO_2)_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

was thus obtained in bright yellow needles, m. p. 99—100° (Found : N = 11·6; S = 12·6. $C_8H_8O_5N_2S$ requires N = 11·5; S = 13·1 per cent.). The substance is readily soluble in alcohol, but sparingly so in cold benzene. It is decomposed when heated with concentrated aqueous potassium hydroxide, some diethylene disulphide being produced. It is unaffected by boiling concentrated hydrochloric acid or by thionyl chloride. Fusion with phosphorus pentachloride at once converts it into 2 : 4-*dinitrophenyl β-chloroethyl sulphide*, $C_6H_3(NO_2)_2{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl$, which crystallises from methyl alcohol in rectangular plates of a deep yellow colour, m. p. 97° (Found : Cl = 13·6. $C_8H_7O_4N_2ClS$ requires Cl = 13·46 per cent.).*

This chloro-compound, when boiled for half an hour with a large excess of sodium ethoxide in alcoholic solution, did not yield the whole of its chlorine in the ionic condition. It does not combine with bromine in chloroform solution. When warmed for a few minutes with fuming nitric acid, it gave a *sulphoxide* which crystallised from methyl alcohol in brilliant yellow needles, m. p. 123° (Found : Cl = 12·15. $C_8H_7O_5N_2ClS$ requires Cl = 12·31 per cent.).

2 : 4-*Dinitrophenyl β-bromoethyl sulphide*, obtained from the corresponding hydroxy-compound by the action of phosphorus tribromide in benzene solution, crystallises from light petroleum in minute, lemon-yellow plates, m. p. 91—92° (Found : Br = 25·9. $C_8H_7O_4N_2BrS$ requires Br = 26·05 per cent.), and gives a *sulphoxide*, lemon-yellow needles from alcohol, m. p. 136° (Found : Br = 24·65. $C_8H_7O_5N_2BrS$ requires Br = 24·75 per cent.).

We wish to thank Messrs. Strange and Graham, Ltd., for the facilities which they have afforded us for this work.

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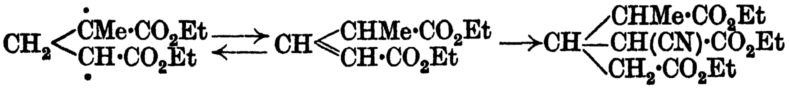
* In estimating halogens by the Robertson method (T., 1915, **107**, 904), the use of 2 grams of sodium perborate is to be recommended in place of 10 c.c. of hydrogen peroxide solution, as being more easily obtained free from chlorides.

CCXII.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part IV. Conditions of Formation by the Cyanoacetic Ester Method of Stable Methanetriacetic Esters.*

By CHRISTOPHER KELK INGOLD and EDWARD ARTHUR PERREN.

IN Part I of this series (this vol., p. 341) attention has been directed to the difficulty which in many instances attends the conversion of the mobile glutaconic esters into derivatives of methanetriacetic acid by condensation with ethyl cyanoacetate, and is to be traced to the permanence of the "normal" forms of the glutaconic esters. One of the purposes of the present paper is to show that by suitably applying the knowledge gathered by Thorpe and his collaborators regarding the conditions controlling the relative stability of the normal and unsaturated forms of the glutaconic esters it is possible to obtain condensation products of the desired type.

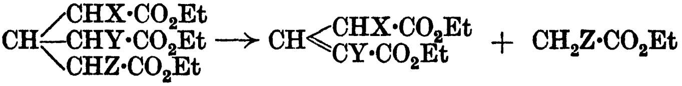
It has been pointed out (*loc. cit.*; Ingold and Thorpe, this vol., p. 493) that equilibrium between and speed of interconversion of the two forms of a glutaconic acid derivative are fundamentally conditioned by substitution in the three-carbon system, and that the permanence of the normal modification is dependent on symmetry. α-Substitution, therefore, since it is unsymmetrical substitution, although it may not much affect dynamic mobility, always tends greatly to reduce the permanence of the normal form and to shift the equilibrium in the direction favouring the unsaturated isomeride, whilst β-substitution, although not seriously altering the static relation between the two forms at equilibrium, invariably effects a considerable reduction in the speed of interconversion. The conditions which most facilitate the condensation of an equilibrated glutaconic ester with ethyl cyanoacetate to form a derivative of methanetriacetic acid are (*a*) that the equilibrium should as far as possible favour the unsaturated modification, (*b*) that the ester should be sufficiently mobile to regenerate the unsaturated form as fast as the condensation process removes it. Hence, of all the simpler, equilibrated esters of the glutaconic series, α-methylglutaconic ester should be that which will most readily react with ethyl cyanoacetate to form a product of the methanetriacetic acid type. Actually this is the case; equilibrated α-methylglutaconic ester (I) condenses with ethyl sodiocyanoacetate to give ethyl ω-cyano-ω′-methylmethanetriacetate (II) in almost quantitative yield :



$$\mathrm{CH_2}\Big<\begin{array}{l}\mathrm{CMe{\cdot}CO_2Et}\\ \mathrm{CH{\cdot}CO_2Et}\end{array} \rightleftarrows \mathrm{CH}\Big<\begin{array}{l}\mathrm{CHMe{\cdot}CO_2Et}\\ \mathrm{CH{\cdot}CO_2Et}\end{array} \longrightarrow \mathrm{CH}\begin{array}{l}\diagup\mathrm{CHMe{\cdot}CO_2Et}\\ -\mathrm{CH(CN){\cdot}CO_2Et}\\ \diagdown\mathrm{CH_2{\cdot}CO_2Et}\end{array}$$

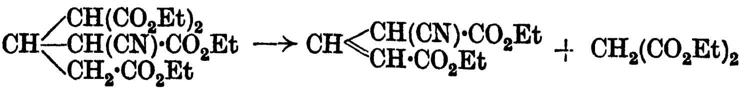
(I.) (II.)

In Part III (this vol., p. 1582) it was pointed out that of the comparatively few methanetriacetic esters which are capable of being *formed* from glutaconic esters by the cyanoacetic ester method a considerable proportion are unstable and decompose completely into smaller molecules under the conditions of their formation. The cause of these decompositions is the reversibility of the Michael reaction; the determining factors affecting particular cases are (largely, at any rate) spatial. Thus, certain methanetriacetic acid derivatives containing two or three branched acetic acid chains attached to the methane carbon atom decompose, as we have shown (*loc. cit.*), according to the equation



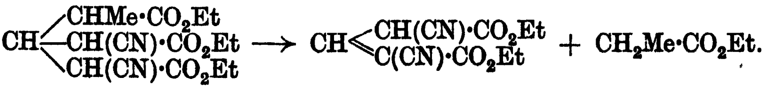
$$\mathrm{CH}\begin{array}{l}\diagup\mathrm{CHX{\cdot}CO_2Et}\\ -\mathrm{CHY{\cdot}CO_2Et}\\ \diagdown\mathrm{CHZ{\cdot}CO_2Et}\end{array} \longrightarrow \mathrm{CH}\Big<\begin{array}{l}\mathrm{CHX{\cdot}CO_2Et}\\ \mathrm{CY{\cdot}CO_2Et}\end{array} + \mathrm{CH_2Z{\cdot}CO_2Et}$$

(a retrograde Michael condensation, therefore) to an extent apparently determined by the space occupied by the branched chains, and therefore by the volumes of the groups X, Y, Z. The greater the volumes of the adjacent residues, the greater is the tendency towards decomposition into smaller molecules. Now, although the exact conditions *necessary and sufficient* to determine this reaction can only be discovered by an extended research, it is apparent from the previous investigation that in methanetriacetic acid derivatives the existence of two branched acetic acid chains is a *necessary* circumstance. That, although necessary, it is not always *sufficient* is proved by the stability of the ester II. Yet, one must observe, if the methyl group in this ester be replaced by a large group, for example, carbethoxyl, decomposition will ensue (with elimination of ethyl malonate) :



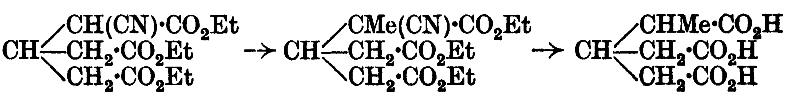
$$\mathrm{CH}\begin{array}{l}\diagup\mathrm{CH(CO_2Et)_2}\\ -\mathrm{CH(CN){\cdot}CO_2Et}\\ \diagdown\mathrm{CH_2{\cdot}CO_2Et}\end{array} \longrightarrow \mathrm{CH}\Big<\begin{array}{l}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{CH{\cdot}CO_2Et}\end{array} + \mathrm{CH_2(CO_2Et)_2}.$$

Moreover, the difference of stability is not due to the impossibility of eliminating a residue, such as $\cdot\mathrm{CHMe{\cdot}CO_2Et}$, as an ester (ethyl propionate) which cannot take part to any appreciable degree in a direct Michael condensation; for the residue in question will be readily extruded if a substituent be introduced into the third acetic acid chain (*loc. cit.*):



$$CH\left\langle\begin{array}{l}CHMe\cdot CO_2Et\\ CH(CN)\cdot CO_2Et\\ CH(CN)\cdot CO_2Et\end{array}\right. \longrightarrow CH\left\langle\begin{array}{l}CH(CN)\cdot CO_2Et\\ C(CN)\cdot CO_2Et\end{array}\right. + CH_2Me\cdot CO_2Et.$$

The ester II, therefore, is one of the few amongst its analogues so constituted that in its preparation one escapes both the inhibiting circumstances ordinarily met with. On complete hydrolysis it yields ω-methylmethanetriacetic acid (V), which may therefore be prepared in quantity by this method; it has already been obtained by Skraup (*Monatsh.*, 1900, **21**, 910) by the degradation of quinine *via* cincholeuponic acid. Skraup also obtained the acid, in sufficient quantity to identify it with the substance derived from quinine, by hydrolysing the crude condensation product of α-methylglutaconic and malonic esters, but in view of the capacity possessed by glutaconic derivatives for yielding products of 1 : 3-addition, no synthesis of this kind can be regarded as a proof of structure. We have, however, definitely established the constitution of the acid, and therefore that of the ester (II), by proving the identity of the acid with that obtained by hydrolysing the ester (IV). This ester is prepared by methylating ethyl ω-cyanomethanetriacetate (III) (compare this vol., p. 352), and its constitution is not open to question.



$$CH\left\langle\begin{array}{l}CH(CN)\cdot CO_2Et\\ CH_2\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{array}\right. \rightarrow CH\left\langle\begin{array}{l}CMe(CN)\cdot CO_2Et\\ CH_2\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{array}\right. \rightarrow CH\left\langle\begin{array}{l}CHMe\cdot CO_2H\\ CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{array}\right.$$

(III.) (IV.) (V.)

With this communication it is proposed to close for the present our examination of the conditions governing the synthesis of the methanepolyacetic acids by the cyanoacetic ester method; to turn on the one hand to other methods of producing these acids, and on the other to what appear to be the logical consequences regarding the circumstances controlling carbon-chain formation in general, of the clues which the investigation has afforded.

EXPERIMENTAL.

Condensation of Ethyl α-Methylglutaconate with Ethyl Cyanoacetate.

Ethyl α-methylglutaconate (9 grams) was added to a suspension in ethyl alcohol of ethyl sodiocyanoacetate prepared by dissolving 1 gram of sodium in 20 grams of ethyl alcohol and adding 5 grams of ethyl cyanoacetate. When the mixture was heated on the steam-bath, the ethyl sodiocyanoacetate rapidly dissolved and another sodium compound separated from the brown solution. After twenty-four hours, water was added, and the products were extracted by means of ether after acidification with hydrochloric acid.

Ethyl ω-Cyano-ω′-methylmethanetriacetate (II).

The extracted esters were separated into neutral and acid portions by washing the ethereal extract with sodium carbonate solution in the usual manner, and the neutral fraction was distilled under diminished pressure. The ester was thus obtained as a colourless oil, b. p. 218—222°/22 mm. The yield was 11 grams, and a further quantity was obtained by esterifying the acid condensation product by means of ethyl alcohol (Found : C = 57·2; H = 7·3. $C_{15}H_{23}O_6N$ requires C = 57·5; H = 7·3 per cent.).

ω-Methylmethanetriacetic Acid (V).

The ester was mixed with an equal volume of cold concentrated sulphuric acid, and, after keeping for one hour, with a similar amount of water. The whole was boiled until carbon dioxide ceased to be expelled, more water was then added, and the boiling was continued for five hours, the condenser being removed from time to time to facilitate the escape of ethyl alcohol. The product of hydrolysis was extracted by pure ether, and was recovered by evaporating the solvent as a colourless syrup, which, on touching with a glass rod, immediately set to a cake of crystals with evolution of heat. It separated from ethyl acetate in prisms, m. p. 138—139° (Found : C = 47·1, H = 6·1. Calc., C = 47·1; H = 5·9 per cent.). Its identity with the acid obtained (this vol., p. 1600) by hydrolysing the methylation product of ethyl ω-cyanomethanetriacetate was conclusively established by directly comparing the two substances and by a mixed-melting point determination.

We are much indebted to Professor J. F. Thorpe for his helpful interest and to the Chemical Society for a large contribution to the cost of this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W.7.
[*Received, September 23rd,* 1921.]

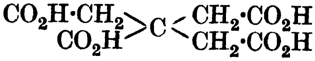
CCXIII.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part V. The Preparation of Carboxymethanetriacetic Acid.*

By CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL.

THE synthesis of the methanepolyacetic acids by the cyanoacetic ester method, although it has been successful in certain directions, is controlled by circumstances which effectively prevent the preparation of some of the desired substances. It has therefore become necessary to discover other methods of synthesis.

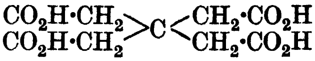
Since the methanepolyacetic acids are required for the preparation of associated alicyclic compounds, the number of methods available is necessarily restricted; when large amounts are needed, the method of production should be both rapid and inexpensive.

*cyclo*Hexane-1 : 1-diacetic acid, the preparation of which in quantity from *cyclo*hexanone and ethyl cyanoacetate has been standardised in this laboratory, on oxidation under conditions which bring about the fission of the *cyclo*hexane ring, might give the C_8-acid (I) and one or both of the two possible C_9-acids (II) and (III):



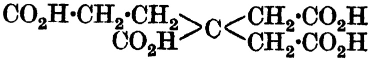
$$\begin{matrix}CO_2H\cdot CH_2\\ CO_2H\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

(I.)



$$\begin{matrix}CO_2H\cdot CH_2\\ CO_2H\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

(II.)



$$\begin{matrix}CO_2H\cdot CH_2\cdot CH_2\\ CO_2H\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

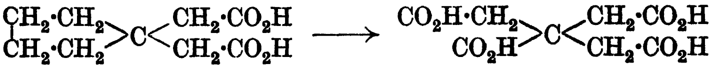
(III.)

Carboxymethanetriacetic acid (I), and methanetetra-acetic acid (II), the preparation of which formed part of the original program of the research (this vol., p. 341), have not yet been obtained, and it would appear that, provided the correct experimental conditions can be found, the oxidation of *cyclo*hexane-1 : 1-diacetic acid should afford an extremely simple and direct method for the production of these substances.

Our experiments have been concerned mainly with the action of hot alkaline permanganate on *cyclo*hexane-1 : 1-diacetic acid, and we have succeeded in producing by this means an acid of the formula $C_9H_{12}O_8$. Unfortunately, however, we have been unable to determine which of the two possible formulæ (II and III) expresses its constitution, for the reason that the conditions of its formation appear to lie between extremely narrow limits, and we have not yet discovered how to standardise them sufficiently to enable a satisfactory quantity of the substance to be prepared. On the other hand, we have found that by employing more concentrated permanganate it is possible to obtain an excellent yield of a tetrabasic acid, $C_8H_{10}O_8$, which can only be the required carboxymethanetriacetic acid (I).

It is fortunate that the handling of bulky solutions, unavoidable in carrying out permanganate oxidations with even moderately large quantities of material, does not constitute a difficulty in the preparation of carboxymethanetriacetic acid by this method; for in the large-scale laboratory recently erected in this College the manipulation of considerable volumes has become an easy matter. The method, therefore, appears to satisfy all the conditions imposed by the object with which it was elaborated.

Carboxymethanetriacetic acid (I) may also be obtained by oxidising *cyclo*pentane-1 : 1-diacetic acid :



$$\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix} \longrightarrow \begin{matrix}CO_2H\cdot CH_2\\ CO_2H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

but an acid $C_9H_{12}O_8$ could not be isolated from the product.

EXPERIMENTAL.

(*A*) *Oxidation of* cyclo*Hexane*-1 : 1-*diacetic Acid.*

A considerable number of experiments have been carried out with a view to obtain information regarding the effect of experimental conditions on the decomposition of *cyclo*hexane-1 : 1-diacetic acid by alkaline permanganate, the variable factors the influence of which has been studied being (*a*) initial concentration of permanganate, (*b*) excess quantity of permanganate, (*c*) temperature, (*d*) time. The experiments were conducted in thermostats and the conditions controlled with all possible care. In this way it was shown that:

(i) within the range covered by the experiments, the two acids described below are the only two substances produced besides carbon dioxide and water.

(ii) by correctly regulating the conditions, carboxymethanetriacetic acid becomes the sole crystalline product.

The Acid $C_9H_{12}O_8$ (II or III).

This acid was isolated from the products of experiments in which a 50 per cent. excess of 3 per cent. potassium permanganate was employed, the temperature being that of the steam-bath and the time allowed fifteen hours. We are unable to make a precise statement of the conditions most favourable to its production, since the yield, although sometimes amounting to 30 per cent. of the theoretical, was extremely variable and appeared to be influenced by some circumstance other than those which we sought to control. The acid was isolated from the solution in the way described in connexion with the preparation of carboxymethanetriacetic acid (below), and was separated from the unchanged *cyclo*hexane-1 : 1-diacetic acid, which always accompanied it, by triturating with cold water (in which the diacetic acid is almost insoluble). It was purified by crystallisation from a mixture of chloroform and ether, from which it separated in dense prisms, m. p. 120° (decomp.) (Found: C = 43·3; H = 5·2. $C_9H_{12}O_8$ requires C = 43·5; H = 4·9 per cent.).

The acid cannot be titrated satisfactorily and in this respect it resembles the carboxymethanetriacetic acid described below; indeed, this appears to be a property of many polybasic aliphatic acids and especially of those which readily form anhydrides. However, the results obtained clearly indicated that the acid was tetrabasic. The acid also resembles carboxymethanetriacetic acid in its extreme solubility in water, its capacity for separating with water of crystallisation, and in the insolubility of its barium salt; there can, we think, be no doubt that the two substances have closely analogous constitutions.

Carboxymethanetriacetic Acid (I).

Carboxymethanetriacetic acid is always formed to some extent when *cyclo*hexane-1 : 1-diacetic acid is oxidised by alkaline permanganate. The limits of successful experiment, however, are not widely separated, as under mild conditions, for example, those made use of in the preparation of the acid $C_9H_{12}O_8$ (above), a considerable quantity of *cyclo*hexanediacetic acid is usually left unattacked, whilst if the conditions be too drastic, for instance, if a 150 per cent. excess of 7 per cent. permanganate be employed at 103° for twenty-four hours, a large proportion of the material will be converted into carbon dioxide and water. The crystalline product in these circumstances consists solely of carboxymethanetriacetic acid, but the yield is correspondingly poor. The following conditions are the best that we have so far found for the preparation of carboxymethanetriacetic acid in quantity.

1·5 Kilograms of potassium permanganate were dissolved in 25 litres of water at 80° contained in a steam-heated, enamelled iron pan, and 106 grams of sodium carbonate followed by 200 grams of *cyclo*hexanediacetic acid were gradually added. The total volume was then made up to 30 litres by the addition of hot water, and the supply of steam entering the jacket of the pan was so regulated that the temperature remained at 80° for ten hours while the solution was continuously stirred in order to prevent the manganese dioxide collecting on the sides and bottom of the pan and disturbing the temperature equilibrium. The steam supply was turned off over-night, but on the next day the stirring and heating were recommenced, and the temperature of the solution was again maintained at 80° for ten hours. On the third day, the cooled solution was acidified by adding 1·5 litres of concentrated hydrochloric acid, and was then treated with a stream of sulphur dioxide until the excess of permanganate had been reduced and the manganese oxides completely dissolved. The clear solution was concentrated to a small bulk, cooled, and filtered. The solid portion was washed with cold water and dried in a vacuum at 100°, but it was found to contain no appreciable quantity of organic matter. The filtrate was evaporated completely, and the residue dried in vacuum-ovens, ground in a mill, and extracted with hot acetone, from which, on evaporation, the acid was obtained as a syrup which gradually set to a hard, crystalline cake. The yield of crude acid was 165 grams (70 per cent. of the theoretical). It is not decreased by a considerable increase in the scale of the experiment.

Purification was effected through the ethyl ester, which was prepared as described below, purified by distillation, and rehydrolysed by boiling with hydrochloric acid until no more alcohol was evolved and then evaporating on a water-bath. The yield of pure acid was 50 per cent. of the theoretical.

The Monohydrate.—The pure acid crystallises from very concentrated aqueous solution in needles, melting with decomposition at 181°, and containing one molecule of water of crystallisation (Found: C = 38·3; H = 4·75. $C_8H_{10}O_8,H_2O$ requires C = 38·1; H = 4·75 per cent.). On keeping in a dry atmosphere, part of the water of crystallisation is rapidly lost.

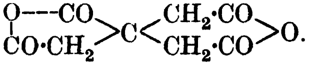
The Anhydrous Acid.—The hydrate was heated for two hours at 120° and the residue recrystallised from a mixture of acetone and chloroform, from which the anhydrous acid separated in minute crystals melting with decomposition at 208—210° (Found: C = 40·7; H = 4·5. $C_8H_{10}O_8$ requires C = 41·0; H = 4·3 per cent.).

The Barium Salts.—The acid forms a very characteristic barium salt, which, although it separates with water of crystallisation, is exceedingly insoluble in hot or cold water and can be precipitated by adding aqueous barium hydroxide to a solution of the ammonium salt even at considerable dilutions. The precipitate, after drying at 95°, consists of the *trihydrate* (Found: Ba = 48·9. $C_8H_6O_8Ba_2,3H_2O$ requires Ba = 49·1 per cent.), but if it be dried to constant weight at 160°, the *monohydrate* will be obtained (Found: Ba = 52·45. $C_8H_6O_8Ba_2,H_2O$ requires Ba = 52·5 per cent.). The *anhydrous* salt is formed when either of the hydrates is heated to constant weight at 220° (Found: Ba = 54·1. $C_8H_6O_8Ba_2$ requires Ba = 54·3 per cent.).

Ethyl Carboxymethanetriacetate.

Carboxymethanetriacetic acid is not readily converted into its tetraethyl ester by the ordinary methods of esterification, and the following process was therefore resorted to. The crude acid (165 grams) was mixed with 400 c.c. of ethyl alcohol and 50 c.c. of concentrated sulphuric acid in a flask fitted with a 10 cm.-fractionating column and a condenser. A stream of ethyl alcohol vapour was passed into the flask, which was kept in an oil-bath at 120° until 4 litres of distillate had collected. The reaction mixture was then cooled and poured into ice-cold water, and the esters were extracted by means of ether, separated from acid products by sodium carbonate solution in the usual manner, and purified by distillation under diminished pressure. In this way 156 grams of the pure ester, b. p. 208°/15 mm. (Found: C = 55·3; H = 7·5. $C_{16}H_{26}O_8$ requires C = 55·5; H = 7·5 per cent.), were obtained together with a small amount of "low fraction," consisting largely of the same substance, and 10 grams of a mixture of acid esters which yielded the same carboxymethanetriacetic acid on hydrolysis.

The Di-anhydride,



$$\begin{array}{l}O{-}{-}{-}CO\\ |\\ CO{\cdot}CH_2\end{array}\!>C<\!\begin{array}{l}CH_2{\cdot}CO\\ CH_2{\cdot}CO\end{array}\!>O.$$

This substance was prepared by boiling the acid (or its monohydrate) with an excess of acetic anhydride for one hour, and distilling off the acetic acid under diminished pressure at 100°. The residue solidified on keeping, and the solid, after recrystallisation from acetone, melted at 223° with slight decomposition. It was insoluble in water, but dissolved slowly in sodium carbonate solution, forming sodium carboxymethanetriacetate (Found: C = 48·1; H = 3·2. $C_8H_6O_6$ requires C = 48·5; H = 3·0 per cent.).

It will be observed that this anhydride melts at a higher temperature than the corresponding acid, a circumstance which is very unusual, but not unknown; two other instances of the same phenomenon are afforded by ββ-dimethylglutaric and camphoric anhydrides.

(*B*) *Oxidation of* cyclo*Pentane*-1 : 1-*diacetic Acid.*

Very little need be said regarding our experiments on the oxidation of *cyclo*pentane-1 : 1-diacetic acid, since the method of working was the same as that already described in connexion with the oxidation of its ring-homologue and the sole product was the carboxymethanetriacetic acid already dealt with. It should be noted, however, that the acid $C_9H_{12}O_8$ appeared not to be produced under any of the conditions used, and also, for it is of theoretical interest in connexion with a modification of the "Spannungstheorie" recently suggested (Ingold, this vol., p. 305), that so far as we could judge there is no considerable difference in the ease of fission by oxidation of the homocyclic rings present in *cyclo*pentane- and *cyclo*hexane-1 : 1-diacetic acids.

We are greatly indebted to Professor J. F. Thorpe for the interest which he has taken in this work and also for much valuable advice. We wish to thank the Chemical Society for a grant which has defrayed a large part of the cost of the investigation.

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CCXIV.—*Dichloroacetates and Chlorobromoacetates from αβ-Dichlorovinyl Ethyl Ether.*

By HOLLAND CROMPTON and PHYLLIS MARY TRIFFITT.

CHLORINE is readily absorbed by αβ-dichlorovinyl ethyl ether at the ordinary temperature. If care is taken to exclude moisture, the product, on heating, or on keeping for some time, breaks up into dichloroacetyl chloride and ethyl chloride,

$$CHCl{:}CCl{\cdot}OEt + Cl_2 = CHCl_2{\cdot}COCl + EtCl.$$

If water is added, or if the product is left exposed to the air, when moisture will be absorbed, on heating or on keeping hydrogen chloride is evolved, and on distillation ethyl dichloroacetate is obtained in almost theoretical yield,

$$CHCl{:}CCl{\cdot}OEt + Cl_2 + H_2O = CHCl_2{\cdot}CO_2Et + 2HCl.$$

The action of bromine on αβ-dichlorovinyl ethyl ether is similar to that of chlorine. With perfectly dry materials and careful exclusion of water, chlorobromoacetyl chloride, b. p. 138—139°, and ethyl bromide are obtained. If free access of moisture is allowed, ethyl chlorobromoacetate, b. p. 174°, $d_{4°}^{22°}$ 1·5890, is produced, along with hydrogen chloride and hydrogen bromide.

From the behaviour of chlorinated and brominated dichlorovinyl ethyl ether with water, it seemed likely that the substitution of alcohols or phenols for water in the above reactions would lead to the production of esters of dichloroacetic and chlorobromoacetic acids. This was found to hold for ethyl and amyl alcohols and for a number of phenols. Aryl dichloroacetates and chlorobromoacetates are usually solids at the ordinary temperature, crystallising readily from the reaction product and obtainable in good yield.

Corresponding aryl dichloroacetates and chlorobromoacetates appear to be isomorphous and to form mixed crystals with one another in all proportions. The melting points of these compounds are also almost identical, the replacement of a chlorine atom in the dichloroacetate by a bromine atom having only a slight effect on the melting point. This is shown in the case of the phenyl derivatives.

Phenyl dichloroacetate, m. p. 48°, b. p. 247·5° (corr.), $d_{4^\circ}^{50^\circ}$ 1·2991.

Phenyl chlorobromoacetate, m.p. 46·5°, b.p. 266° (corr.), $d_{4^\circ}^{50^\circ}$ 1·5311.

The melting points are those determined in the ordinary way. The solidifying or freezing points of these compounds, and of their mixtures with one another in varying proportions, are given in the following table:

Molecular percentage of		Freezing Points.	
Dichloroacetate.	Chlorobromoacetate.	Obs.	Cal.
100	0	46·25°	—
91·7	8·3	45·9	46 0
83·1	16·9	45·5	45·8
75·3	24·7	45·0	45·6
56·3	43·7	44·7	45·1
31·9	68·1	44·2	44·5
20 0	80·0	44·05	44·2
9 8	90·2	43·9	44·0
0	100	43·7	—

The numbers given in the last column are those calculated on the assumption that the freezing points of the mixtures, when plotted against molecular percentages, lie on a straight line connecting the freezing points of the two components. As is usual in cases of this kind, the observed values are slightly lower than the calculated.

In the other cases examined it was not found possible to detect a difference between the melting points of corresponding aryl compounds determined in the usual way. These cases were:

p-Tolyl dichloroacetate and chlorobromoacetate, m. p. 58°.

β-Naphthyl dichloroacetate and chlorobromoacetate, m.p. 92—93°.

Quinol bisdichloroacetate and bischlorobromoacetate, m. p. 123—124°.

The corresponding compounds can be mixed with one another in any proportion with no appreciable effect on the melting point.

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[*Received, October 12th*, 1921.]

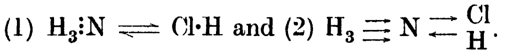
CCXV.—*Valency and Co-ordination.*

By Samuel Henry Clifford Briggs.

As an attempt has recently been made to show that Werner's conception of co-ordination is of a more fundamental character than hitherto supposed (Briggs, *Phil. Mag.*, 1921, **42**, 448), it seems desirable to refer to some criticisms of Werner's views brought forward by Rhodes (*Chem. News*, 1921, **122**, 85, 97) and by Friend (this vol., p. 1042).

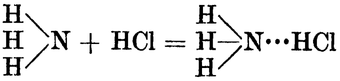
(1) Rhodes objects to Werner's formula for ammonium chloride, chiefly on the ground that the position of the chlorine in $(NH_4)Cl$ suggests instability, the chlorine being combined with the complex as a whole rather than with an individual atom in the complex. When it is remembered, however, that the ammonium radicle and the chloride ion possess equal and opposite electrical charges, the stability of the compound is not difficult to understand.

Friend suggests that ammonium chloride exists in two forms



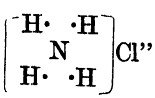
$$(1)\ H_3{:}N \rightleftharpoons Cl{\cdot}H \text{ and } (2)\ H_3 \rightrightarrows N \begin{smallmatrix}\rightarrow Cl\\ \leftarrow H\end{smallmatrix}.$$

According to Werner ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd. ed., p. 248) ". . . die Entstehung von Chlorammonium folgendermassen wiederzugeben ist



$$\begin{matrix}H\\H\\H\end{matrix}\!>\!N + HCl = \begin{matrix}H\\H\\H\end{matrix}\!\rightarrow\!N\cdots HCl$$

. . . und da es unwahrscheinlich ist dass ein Wasserstoffatom durch einen anderen Affinitätsbetrag an Stickstoff gekettet ist als die drei anderen, so wird sich im Affinitätsausgleich ein Endzustand herausbilden, bei dem sämtliche Wasserstoffatome durch gleiche Affinitätsbeträge an dem Stickstoff gebunden sind. Das Ammonium ist hiernach ein komplexes Radical, NH_4, in dem ein zentrales Stickstoffatom vier Wasserstoffatome jedes mit gleichem Affinitätsbetrag, bindet . . . . Strukturchemisch ist das Chlorammonium deshalb durch folgendes Symbol wiederzugeben



$$\left[\begin{matrix}H\cdot & & \cdot H\\ & N & \\ H\cdot & & \cdot H\end{matrix}\right]Cl\text{"}\quad (2)$$

The existence of ammonium chloride in two forms is therefore quite possible on Werner's theory, but Werner's formula (2) appears preferable to Friend's second formula, because the chlorine atom is ionisable, whereas the hydrogen atoms are not.

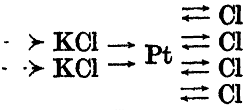
(2) In the writer's opinion, Werner's formula for the carbonatopentamminecobaltic salts is not a violation of the co-ordination theory, as suggested by Friend. One of the negatively-charged oxygen atoms of the carbonate ion is linked to the cobalt and the other charged atom is not linked up and will therefore be analogous to a charged atom (anion) outside the complex, as shown in Werner's formula. The carbonato-radicle, however, will not give free carbonate ions in solution owing to the non-ionisable union of *one* oxygen atom with the central cobalt atom.

(3) The shell theory suggested by Friend for complex compounds is open to criticism on the following grounds.

(*a*) If the ammonia molecules in $Co(6NH_3)Cl_2$ and $(Co6NH_3)Cl_3$ are not attached to the cobalt atom, but are linked up to each other to make a shell, there is no apparent reason for the great difference in stability of the compounds. But if they are attached to the cobalt as required by Werner's theory, it follows from the electrical theory of the atom that the cobaltic compound is more stable than the cobaltous salt, as is actually the case (Briggs, T., 1917, **111**, 253).

(*b*) On Friend's shell theory, there is no explanation of Werner's maximum co-ordination numbers 4, 6, 8 (and 12). The writer has shown, however, that if the co-ordinated atoms or groups are directly attached to the central atom as required by Werner, then the maximum co-ordination numbers follow on geometrical grounds from Rutherford's theory of the atom with a positive nucleus (T., 1919, **115**, 278).

(*c*) Friend's shell theory, when applied to the salts of complex acids, requires isomerism due to differences in the points of attachment of the positive atoms. The writer held the view that such isomerism might be possible in a paper on duplex affinity published some years ago, formula I being given to potassium platinichloride (T., 1908, **93**, 1564). In later papers, the theory was developed further on the assumption that positive affinity is a tendency to lose electrons, and negative affinity a tendency to attract electrons. With such an assumption we can only expect that in the complex ion $PtCl_6''$ the chlorine atoms will all become electrically equal, and that consequently the potassium atoms will be united to the complex as a whole, as seen in formula II and as required by Werner's theory, instead of to distinct chlorine atoms, as shown in formula I and as is also required by Friend's theory. Stereoisomerism should not therefore be possible.



(I.)

$$\begin{array}{l} \\ \dashrightarrow \mathrm{KCl} \rightarrow \\ \dashrightarrow \mathrm{KCl} \rightarrow \\ \\ \end{array} \mathrm{Pt} \begin{array}{l} \rightleftarrows \mathrm{Cl} \\ \rightleftarrows \mathrm{Cl} \\ \rightleftarrows \mathrm{Cl} \\ \rightleftarrows \mathrm{Cl} \end{array}$$

$$\dashrightarrow \mathrm{K}_2^{\bullet}(\mathrm{Pt}^{\bullet\bullet\bullet\bullet} \longleftarrow \mathrm{Cl}_6' \dashrightarrow)$$

(II.)

The question can, however, be decided only by experimental investigation, and the writer has been engaged for some years in the study of such supposed cases of isomerism. It has been already shown that Marignac's second form of potassium stannifluoride is potassium hydroxopentafluorostanneate, $K_2(SnF_5OH)$ (*Zeitsch. anorg. Chem.*, 1913, **82**, 441), that Locke and Edwards's second form of potassium ferricyanide is a compound of the formula $3K_3Fe(CN)_6,K_2[Fe(CN)_5H_2O]$, and that the second form of potassium ferrocyanide observed by the writer is the ordinary ferrocyanide containing a trace of aquopentacyanoferroate (T., 1920, **117**, 1026). The remaining cases of the two aquopentachlororutheniates and the two hexachlororutheneates are now being investigated. It has been found that the formula for the first pair of isomerides is not K_2RuCl_5,H_2O, but $2K_2RuCl_5,3H_2O$, and it will be shown in a subsequent paper that these can be brought into agreement with Werner's theory. The existence of two salts of the formula K_2RuCl_6 appears doubtful, but the investigation is not yet completed.

(*d*) The difficulty of Friend's shell theory, and indeed of all other valency theories in dealing with strong electrolytes, is apparent if we consider a crystal of sodium chloride in which every sodium ion is surrounded by six chloride ions, and every chloride ion by six sodium ions. It is difficult to imagine a system of two interpenetrating shell lattices, one made up of positively charged sodium atoms linked to each other, and the other of negatively charged chlorine atoms united together. On the other hand, if we write a valency formula with each sodium ion united to six chloride ions, and each chloride ion linked to six sodium ions, as is actually the case, then we must either assume that chlorine and sodium are both sexavalent, or that they each possess six partial valencies, the six being equal to one whole valency. Werner's co-ordination theory is much more satisfactory than any valency theory in this respect, and c n be applied to such crystal structures (Pfeiffer, *Zeitsch. anorg. Chem.*, 1915, **92**, 376; 1916, **97**, 161).

(4) Friend's free valency and residual valency and Thomson's ionised valency and non-ionised valency really represent two extreme types of combination, as is emphasised by Friend (*loc. cit.*, p. 1043) (compare Briggs, T., 1917, **111**, 267). The same argument applies equally to Langmuir's clean-cut division of valency into

electrovalence, in which the charged atoms are held together by electrostatic force, and *co-valence*, in which the atoms are united owing to the sharing of electrons. Since the electrons are united to the kernel of an atom by electrostatic force, it would appear that electrostatic attraction between two charged atoms, that is, electrovalence, involves the sharing of electrons, and the distinction between electrovalence and co-valence is therefore one of degree rather than of kind. Co-valence represents a condition in which electrons are shared equally between two atoms, and electrovalence a condition of unequal sharing, the more unequal the sharing of the electrons the greater the tendency of the compound to undergo electrolytic dissociation.

[*Received, October 12th*, 1921.]

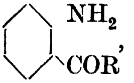
CCXVI.—*Studies in the* n-*Butyl Series. Part I. Aryl* n-*Propyl Ketones.*

By GILBERT T. MORGAN and WILFRED JOHN HICKINBOTTOM.

THE industrial development during recent years of a fermentation yielding *n*-butyl alcohol has rendered available considerable amounts of this alcohol, for which sufficient use has not hitherto been found. A consideration of the problem of the utilisation of this product leads to the conclusion that the solution lies in the employment of derivatives of *n*-butyl alcohol rather than in its use as a substitute for fusel oil. It is from this point of view that we have examined the properties of certain *n*-butyl compounds derived by practicable processes from *n*-butyl alcohol.

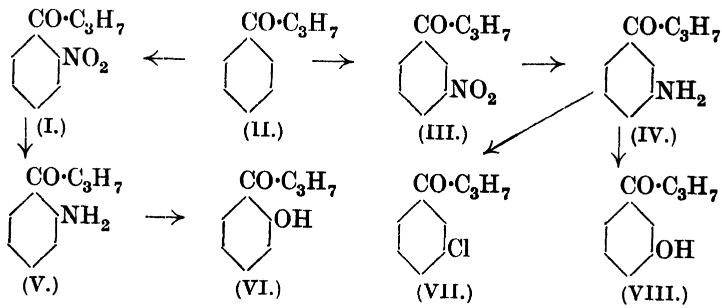
The influence of butyl and butyryl groups in enhancing the odour of chemical substances is well known, and aryl derivatives containing these osmophoric radicles have been prepared and examined. On comparing the odours of the substituted *n*-butylbenzene with those of the corresponding derivatives of phenyl *n*-propyl ketones, it is noticed that the odour diminishes in intensity on passing from the hydrocarbon to the ketone. This is particularly noticeable with the nitro-derivatives. 3-*Nitrophenyl* n-*propyl ketone*, for instance, is almost inodorous, whilst the nitro-*n*-butylbenzenes and 2-*nitro*-1 : 4-*di*-n-*butylbenzene* have characteristic odours. Orientation has its effect, for 2-*nitrophenyl* n-*propyl ketone* has a pleasant odour, which is, however, less fragant than that of the corresponding nitro-derivative of *n*-butylbenzene.

This contrast is not in accordance with the osmophoric theory of Rupe and Majewski (*Ber.*, 1900, **33**, 3401; compare also Klimont, " Die Synthetische und Isolierten Aromatica "),' for it might be expected that the presence of two osmophores, —CO·CH_2— and —NO_2, would give rise to a substance having an odour at least as intense as that of the nitrohydrocarbon. This anomaly is explicable on the assumption that in the aromatic series the effect of an osmophoric grouping is variable, depending, among other factors, on the presence of other osmophores in the molecule and also on their relative positions, so that the odour of a compound containing more than one osmophoric group in its molecule may be either increased or diminished as the orientation of the substituent varies. This influence of orientation is illustrated by a comparison of the odours of various derivatives of phenyl *n*-propyl ketone. Substitution in the *meta*-position yields, as a rule, substances with faint odours, whilst the corresponding *ortho*-compounds generally possess powerful and characteristic odours. It is noteworthy that 2-aminophenyl *n*-propyl ketone, which is an odoriferous substance, contains the grouping characteristic of methyl anthranilate,

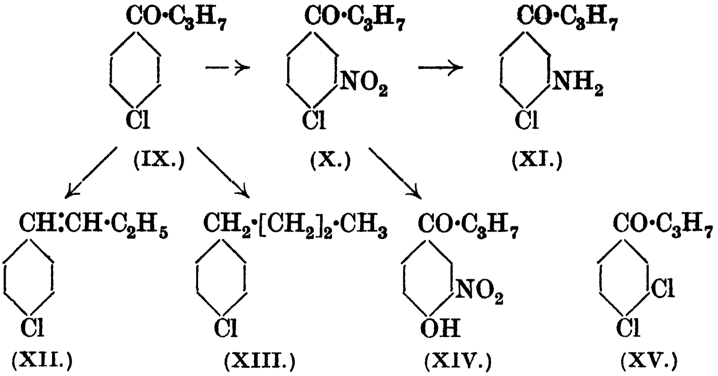


, where R = C_3H_7 or ·O·CH_3 (compare Rupe and Majewski, *Ber.*, 1900, **33**, 3401).

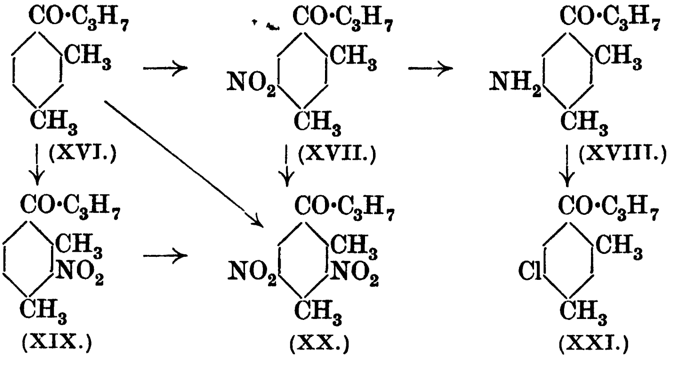
Butyryl chloride was condensed in turn with benzene, chlorobenzene, and *m*-xylene; the resulting ketones were converted successively into their nitro- and amino-derivatives. In the case of phenyl *n*-propyl ketone (II) nitration follows the *meta*-law of substitution, the *meta*-nitro-compound (III) is the main product, but the formation of a small proportion of the *ortho*-nitro-derivative (I) was noticed.



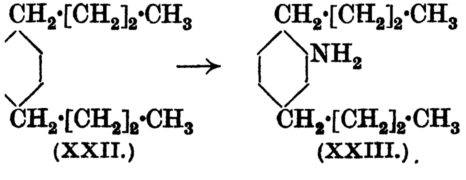
With p-*chlorophenyl* n-*propyl ketone* (IX) the nitro-group enters exclusively the *ortho*-position with respect to chlorine, yielding 4-*chloro*-3-*nitrophenyl* n-*propyl ketone* (X).



In the case of *m*-4-xylyl *n*-propyl ketone (butyro-2 : 4-dimethylphenone, XVI), nitration occurs as with the parent aromatic hydrocarbon, *m*-xylene; the main product is 6-*nitro*-m-4-*xylyl* n-*propyl ketone* (XVII), whereas 2-*nitro*-m-4-*xylyl* n-*propyl ketone* (XIX) is formed in smaller proportion. Further nitration leads to 2 : 6-*dinitro*-m-4-*xylyl* n-*propyl ketone* (XX).



In the foregoing condensations to form mixed ketones the introduction of the butyryl group into the benzene ring through the agency of the Friedel and Crafts reaction occurs much more smoothly than the substitution of a butyl group for chlorine by the Fittig reaction in the formation of p-*di*-n-*butylbenzene* (XXII) from *p*-dichlorobenzene.



Accordingly, the mixed ketones have been submitted to a more detailed examination.

EXPERIMENTAL.

I. *Phenyl* n-*Propyl Ketone.*

Phenyl *n*-propyl ketone was prepared in a 69 per cent. yield by the interaction of *n*-butyryl chloride * and an excess of benzene in presence of aluminium chloride. Phenyl *n*-propyl ketone was characterised by its p-*nitrophenylhydrazone*, which separated from glacial acetic acid in orange-red, prismatic needles having a metallic blue reflex; it melted at 163° (Found: N = 15·13. $C_{16}H_{17}O_2N_3$ requires N = 14·84 per cent.).

1. *Nitration in Acetic Anhydride. 3-Nitrophenyl* n-*Propyl Ketone* (III).—Phenyl *n*-propyl ketone (5·2 grams) was cautiously added with continuous stirring to 33 grams of fuming nitric acid mixed with 32 grams of acetic anhydride, the temperature being maintained below 5°. After half an hour, the nitration mixture was poured on to crushed ice, when crude 3-nitrophenyl *n*-propyl ketone was precipitated as a white, curdy solid, which was pressed from oily by-products. The nitrated ketone separated from warm alcohol in white, brittle plates melting at 61° (Found: C = 61·73; N = 7·53. $C_{10}H_{11}O_3N$ requires C = 62·15; N = 7·25 per cent.). It was not readily soluble in light petroleum or cold alcohol, but more readily so in ether or chloroform. 3-Nitrophenyl *n*-propyl ketone was oxidised to *m*-nitrobenzoic acid on heating with chromic acid or potassium permanganate in presence of dilute sulphuric acid; it yielded a *phenylhydrazone* crystallising from alcohol in orange-red masses of small needles melting at 103°. The p-*nitrophenylhydrazone* was deposited from warm glacial acetic acid in minute, pale yellow crystals melting at 205° (Found: N = 17·28. $C_{16}H_{16}O_4N_4$ requires N = 17·07 per cent.).

2-*Nitrophenyl* n-*Propyl Ketone* (I).

The oily filtrates and washings from the 3-nitro-compound were repeatedly extracted with ether to remove the liquid product of the nitration. The ethereal extract was washed with aqueous sodium hydroxide solution and the solvent evaporated. The residual oil contained a mixture of the 2- and 3-nitro-compounds, from which the greater part of the solid isomeride was removed by freezing. There was not sufficient material available to attempt the lengthy fractionation under diminished pressure which appeared necessary to isolate the *ortho*-nitro-compound in a pure state, and recourse was made to the difference in behaviour of the isomerides with *p*-nitrophenylhydrazine. Crude 2-nitrophenyl *n*-propyl ketone was heated in a boiling water-bath with three-fifths of its weight of *p*-nitrophenylhydrazine in alcoholic solution. A dark red oil resulted which slowly deposited the *p*-nitrophenylhydrazone of the 3-nitro-compound as a reddish-yellow solid. The separation was hastened by treatment with dry ether, when, on submitting the residue to distillation in a current of steam, a pale yellow oil passed over, which was subjected to further treatment with *p*-nitrophenylhydrazine. It was finally purified by two steam distillations in presence of dilute hydrochloric acid. By these means *2-nitrophenyl* n-*propyl ketone* was obtained as a pale yellow oil having a sweet odour resembling to some extent that of nitrobenzene (Found: N = 7·01. $C_{10}H_{11}O_3N$ requires N = 7·25 per cent.).

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* Our thanks are due to Captain Desborough, of the Royal Naval Cordite Factory, for the *n*-butyl alcohol required in this investigation.

In the nitration of phenyl *n*-propyl ketone with nitric acid and acetic anhydride, the yield of mixed nitro-compounds after removing *iso*nitroso-compounds and oxidation products amounted to 97—98 per cent. of the calculated amount.

2. *Nitration in Sulphuric Acid.*—A mixture of 1·1 to 1·2 molecular proportions of nitric acid (*d* 1·42) and concentrated sulphuric acid (18 grams) was added with continuous stirring to phenyl *n*-propyl ketone (5·4 grams) dissolved in 60 grams of concentrated sulphuric acid, the temperature being maintained below 5° throughout the operation. The mixture was left at 0° for about two hours and then poured on to ice. The isolation of 3-nitrophenyl *n*-propyl ketone was effected as in the preceding preparation.

3-Aminophenyl n-*propyl ketone* (IV), obtained in good yield by the reduction of the corresponding nitro-compound with zinc dust and ammonium chloride in aqueous alcoholic solution, was purified by fractionation under diminished pressure; it distilled over as a pale yellow, viscous oil at 194—197°/29—30 mm. and solidified to a white mass of crystals melting at 27—28° (Found: N = 8·30. $C_{10}H_{13}ON$ requires N = 8·59 per cent.).

The *hydrochloride* separated from its concentrated solution in hydrochloric acid in masses of colourless needles, but was hydrolysed in aqueous solution. The *zincichloride* was precipitated as a white, sparingly soluble mass by the addition of an aqueous solution of zinc chloride to a suspension of the base. The *picrate* separated from warm benzene in bright yellow nodules or rosettes of needles melting at 132—133° (Found: N = 14·44. $C_{10}H_{13}ON,C_6H_3O_7N_3$ requires N = 14·28 per cent.).

3-Acetylaminophenyl n-*propyl ketone*, prepared by warming the base with acetic anhydride, separated from a mixture of benzene and light petroleum in plates melting at 71·5—72·5° (Found: N = 7·02. $C_{12}H_{15}O_2N$ requires N = 6·83 per cent.).

3-*Benzoylaminophenyl* n-*propyl ketone* separated from warm aqueous alcohol in small, white crystals melting at 103—104° (Found: N = 5·17. $C_{17}H_{17}O_2N$ requires N = 5·24 per cent.).

n-*Butyrophenone*-3-*azo*-β-*naphthol*, obtained by coupling 3-diazophenyl *n*-propyl ketone chloride with β-naphthol in alkaline solution, crystallised from warm alcohol in small, red needles having a faint green reflex (m. p. 127—128°) (Found: N = 9·05. $C_{20}H_{18}O_2N_2$ requires N = 8·80 per cent.). It gave a crimson coloration in concentrated sulphuric acid.

n-*Butyrophenone*-3-*azo*-β-*naphthylamine*, produced as in the preceding preparation, using an alcoholic solution of β-naphthylamine, crystallised from warm glacial acetic acid in orange-red plates or scales having a coppery lustre, or on slow cooling in small, acicular plates arranged in clusters. It melted at 149—150° (Found: N = 13·51. $C_{20}H_{19}ON_3$ requires N = 13·25 per cent.). This *azo*-β-*naphthylamine* developed in concentrated sulphuric acid a violet-blue coloration, changing to red and brown on dilution. Concentrated hydrochloric acid in glacial acetic acid gave rise to a bright red coloration.

n-*Butyrophenone*-3-*azoresorcinol*.—The diazotised amino-ketone was coupled with resorcinol in either aqueous or alcoholic solution in presence of sodium acetate, when the crude *azo*-compound separated. It was purified by precipitation from its solution in dilute sodium hydroxide and finally by crystallisation from warm benzene, when it separated as an orange-red powder melting at 144° (Found: N = 10·10. $C_{16}H_{16}O_3N_2$ requires N = 9·86 per cent.). A small amount of another *azo*-compound was obtained, which was insoluble in aqueous alkalis, but soluble in alcoholic potassium hydroxide. It separated from alcohol as a bright red, sparingly soluble powder. Sulphuric acid developed a red coloration.

3-*Hydroxyphenyl* n-*Propyl Ketone* (VIII).—On boiling the diazotised solution from 3-aminophenyl *n*-propyl ketone with an excess of diluted sulphuric acid, 3-*hydroxyphenyl* n-*propyl ketone* separated as a dark oil, becoming solid on cooling; it was purified by solution in dilute sodium hydroxide and precipitation with acid, followed by crystallisation from warm light petroleum. It crystallised from a mixture of benzene and light petroleum in white, rhombic plates melting at 63° (Found: C = 73·10; H = 7·46. $C_{10}H_{12}O_2$ requires C = 73·13; H = 7·38 per cent.). 3-Hydroxyphenyl *n*-propyl ketone, which has only a faint, pleasant, phenolic odour, coupled with diazotised *p*-nitroaniline to yield a red *azo*-compound.

The p-*nitrophenylhydrazone* of 3-hydroxyphenyl *n*-propyl ketone crystallised from benzene in orange-yellow needles melting at 160° (Found: N = 14·17. $C_{16}H_{17}O_3N_3$ requires N = 14·04 per cent.).

3-*Chlorophenyl* n-*propyl ketone* (VII), an almost colourless oil volatile in steam, was obtained from the corresponding amino-compound by the Sandmeyer reaction. Its odour resembled that of 4-chlorophenyl *n*-propyl ketone (IX), but was less intense (Found: Cl = 19·15. $C_{10}H_{11}OCl$ requires Cl = 19·42 per cent.).

The p-*nitrophenylhydrazone* separated from glacial acetic acid in minute, dull yellow crystals melting at 138° (Found: N = 13·58. $C_{16}H_{16}O_2N_3Cl$ requires N = 13·23 per cent.).

2-*Aminophenyl* n-*Propyl Ketone* (V).—By reducing 2-nitrophenyl *n*-propyl ketone (I) with zinc dust and ammonium chloride in boiling alcoholic solution, this amine was obtained as a pale yellow oil, volatile in steam and possessing a characteristic and pleasant odour when dilute. On adding concentrated hydrochloric acid to the base, the *hydrochloride* separated in clusters of white, prismatic needles melting at 160—162° to a dark red liquid. It darkened a few degrees below its melting point (Found: N = 6·95; Cl = 17·75. $C_{10}H_{13}ON,HCl$ requires N = 7·01; Cl = 17·76 per cent.). The amine was readily obtained by the reduction of the liquid product of the nitration of phenyl *n*-propyl ketone. On distilling the mixture of amines in a current of steam, the *ortho*-compound passed over the more readily, and was obtained pure by crystallising its hydrochloride two or three times from concentrated hydrochloric acid.

The amine was diazotised readily in dilute hydrochloric acid solution, and on pouring the solution of the diazonium salt into alkaline β-naphthol the *azo-β-naphthol* separated as a bright red powder, which crystallised from warm alcohol in bright red masses of small crystals having a faint metallic reflex. It melted at 154—155° (Found: N = 9·10. $C_{20}H_{18}O_2N_2$ requires N = 8·80 per cent.). The *azo*-compound developed a violet coloration in concentrated sulphuric acid.

On boiling a solution of the diazotised amine with excess of dilute sulphuric acid, 2-*hydroxyphenyl* n-*propyl ketone* (VI) separated as a pale yellow, viscous liquid, which was purified by solution in alkali followed by distillation in a current of steam (Found: C = 73·24; H = 7·13. $C_{10}H_{12}O_2$ requires C = 73·13; H = 7·39 per cent.).

II. 4-*Chlorophenyl* n-*Propyl Ketone* (IX).

n-Butyryl chloride (30 grams) was added gradually with continuous stirring to 83 grams of chlorobenzene mixed with freshly-prepared aluminium chloride (35 grams), the temperature being maintained at 40—60°. After four hours, the product was poured on to ice and the pale yellow oil, having been washed with aqueous sodium hydroxide solution, was distilled, when it gave a colourless fraction at 253—254° (uncorr.) which solidified on cooling to a mass of crystalline and practically pure 4-*chlorophenyl* n-*propyl ketone* (yield 72 per cent.); this product separated from alcoholic solution in white, soft, tabular crystals melting at 36° (Found: Cl = 19·29. $C_{10}H_{11}OCl$ requires Cl = 19·42 per cent.). The ketone, which was soluble in the common organic media, was characterised by a pleasant odour more powerful than that of phenyl *n*-propyl ketone.

Oxidation of 4-chlorophenyl *n*-propyl ketone with sodium dichromate and dilute sulphuric acid gave *p*-chlorobenzoic acid, thereby establishing the orientation of the chlorine substituent with respect to the ketonic group.

The *phenylhydrazone* crystallised from alcohol in white, slender needles melting at 85° (Found: N = 9·20. $C_{16}H_{17}N_2Cl$ requires N = 10·27 per cent.). This hydrazone was found to be unstable, a pure specimen becoming converted into a dark brown tar after one month in a closed tube.

The p-*nitrophenylhydrazone* separated from a mixture of benzene and alcohol in small, yellow crystals melting at 173—174° (Found: N = 13·39. $C_{16}H_{16}O_2N_3Cl$ requires N = 13·23 per cent.).

Reduction of 4-Chlorophenyl n-*Propyl Ketone.*

(*a*) 4-*Chloro*-n-*butylbenzene*.—The reduction was carried out at 80—100° with hydrochloric acid and amalgamated zinc, according to Clemmensen's method for the reduction of ketones to hydrocarbons (*Ber.*, 1913, **46**, 1838). After twelve hours, the insoluble, yellow oil was removed and distilled in a current of steam. In the distillate crude 4-chloro-*n*-butylbenzene (XIII) was obtained, which was fractionally distilled after being separated and dried. The main distillate was collected at 225—228°/761 mm. as a colourless, refractive liquid stable to cold neutral permanganate solution and possessing a powerful odour of anise (Found: Cl = 20·72. $C_{10}H_{13}Cl$ requires Cl = 21·03 per cent.).

4-*Chlorobutenylbenzene* (XII).—In the reduction of the ketone by Clemmensen's method a small quantity of an unsaturated compound was usually obtained, the yield of which was increased by continuing the reduction for a shorter period or by working at a lower temperature. Under these conditions a mixture of 4-chlorobutenylbenzene and 4-chloro-*n*-butylbenzene was obtained in the fraction distilling between 225° and 240°. As the difference in the boiling points of the two substances was inconsiderable, and as the quantity of available material did not permit of a systematic fractionation, evidence of the presence in the mixture of 4-chlorobutenylbenzene was obtained by converting the compound into its dibromide. That portion of the crude reaction product which was volatile in steam was suspended in water and treated with bromine until there was no further absorption. The heavy oil which resulted, having been treated with sodium sulphite solution, was distilled in steam, when a pasty, non-volatile residue (*b*) was obtained on cooling. The liquid portion volatile in steam was separated by distillation into 4-chloro-*n*-butylbenzene (*a*) and a liquid (*c*) boiling with decomposition above 230° and having a fragrant odour of hyacinths. Since the liquid (*c*) contained bromine and yielded 4-*chlorobutenylbenzene* on boiling with anhydrous pyridine for seven hours, it was probably 4-*chlorobromobutylbenzene.*

4-Chlorobutenylbenzene, a colourless, refractive liquid boiling at 234—237°/749 mm., had an odour resembling that of the saturated hydrocarbon (*a*), except that it was less pronounced and somewhat alliaceous (Found: $Cl = 21{\cdot}16$. $C_{10}H_{11}Cl$ requires $Cl = 21{\cdot}28$ per cent.).

(*b*) 4-*Chloro-αβ-dibromo-*n*-butylbenzene.*—The pasty residue (*b*) obtained in the foregoing steam distillation was drained and crystallised from alcohol, when the purified dibromide separated in transparent prisms melting at 72° (Found: $AgCl+AgBr = 159{\cdot}6$. $C_{10}H_{11}ClBr_2$ requires $AgCl+AgBr = 159{\cdot}0$ per cent).

The reduction of 4-chlorophenyl *n*-propyl ketone with amalgamated zinc and hydrochloric acid gave a varying proportion of a vitreous residue, not volatile in steam. By substituting for aqueous hydrochloric acid a solution of one part of concentrated hydrochloric acid in two parts of alcohol, the amount of by-product was increased. The substance was only sparingly soluble in alcohol, but more readily so in benzene or light petroleum. It melted indefinitely at 55—60° and was presumably a *polymeride* of 4-chlorobutenylbenzene.

4-*Chloro-3-nitrophenyl* n-*Propyl Ketone* (X).—It was found necessary to carry out the nitration of 4-chlorophenyl *n*-propyl ketone at a temperature not exceeding —5°, in order to reduce the tendency to oxidation.

4-Chlorophenyl *n*-propyl ketone (2 grams) dissolved in 18 grams of sulphuric acid (*d* 1·84) was cautiously added to a mixture of 15 grams of nitric acid (*d* 1·42) and 36 grams of concentrated sulphuric acid, cooled to —12° and constantly stirred. After the ketone had been added, the nitration mixture was left for a period of ten to thirty minutes and then poured on to crushed ice. The white, curdy solid, after being washed with water and sodium carbonate solution, was purified by crystallisation from alcohol, when it separated in white plates melting at 53° (Found: N = 6·34; Cl = 15·25. $C_{10}H_{10}O_3NCl$ requires N = 6·15; Cl = 15·58 per cent.).

4-*Chloro-3-nitrophenyl* n-*propyl ketone* was faintly odorous, and was sparingly soluble in light petroleum or cold alcohol, but dissolved more readily in ether. On oxidation with aqueous chromic acid solution in presence of sulphuric acid, 4-chloro-3-nitrobenzoic acid (m. p. 180°) was obtained.

The *phenylhydrazone* separated from alcohol in acicular, golden yellow crystals melting at 116—117° (Found: N = 12·91. $C_{16}H_{16}O_2N_3Cl$ requires N = 13·23 per cent.).

The p-*nitrophenylhydrazone*, obtained as a bright yellow, crystalline powder, melted at 215° (Found: N = 15·53. $C_{16}H_{15}O_4N_4Cl$ requires N = 15·45 per cent.).

On heating 4-chloro-3-nitrophenyl *n*-propyl ketone with phosphoric acid at 150—160°, no evidence was obtained of the fission of the butyryl group, the bulk of the substance being recovered unchanged (compare Klages and Lickroth, *Ber.*, 1899, **32**, 1563), excepting for a trace of 3-*nitro-4-hydroxyphenyl* n-*propyl ketone* (XIV), which was obtained more readily on heating the nitrochloro-compound with eighty times its weight of 6 per cent. aqueous potassium hydroxide solution. This nitrophenolic substance was obtained from boiling light petroleum in pale yellow needles melting at 46° (Found: N = 6·71. $C_{10}H_{11}O_4N$ requires N = 6·70 per cent.); it was readily soluble in the ordinary organic solvents with the exception of light petroleum.

The p-*nitrophenylhydrazone*, separating from glacial acetic acid in masses of orange crystals, melted at 203—204° (Found: N = 16·50. $C_{16}H_{16}O_5N_4$ requires N = 16·27 per cent.).

4-*Chloro-3-aminophenyl* n-*propyl ketone* (XI), obtained in good yield by the reduction of the corresponding nitro-compound in alcoholic solution with zinc dust and a trace of ammonium chloride, crystallised from alcohol or warm light petroleum in white, shining plates melting at 97° (Found: N = 7·37. $C_{10}H_{12}ONCl$ requires N = 7·09 per cent.).

The *hydrochloride* separated from warm dilute hydrochloric acid in colourless needles, sparingly soluble in water (Found: HCl = 15·23. $C_{10}H_{12}ONCl,HCl$ requires HCl = 15·58 per cent.).

The diazo-solution from the foregoing hydrochloride, when poured into alkaline β-naphthol, yielded the red *azo-β-naphthol*, which crystallised from glacial acetic acid in red, prismatic needles having a green reflex (m. p. 153°) and developed a reddish-purple coloration with concentrated sulphuric acid (Found: N = 8·16. $C_{20}H_{17}O_2N_2Cl$ requires N = 7·94 per cent.).

3 : 4-*Dichlorophenyl* n-*propyl ketone* (XV), prepared from 4-chloro-3-aminophenyl *n*-propyl ketone by the Sandmeyer reaction, was isolated by distillation in steam and obtained as a colourless oil which could not be induced to crystallise. The odour of this compound was faintly reminiscent of anise and resembled that of 4-chlorophenyl *n*-propyl ketone, although not so intense. 3 : 4-Dichlorophenyl *n*-propyl ketone was characterised by its p-*nitrophenylhydrazone*, which separated from warm glacial acetic acid in bright yellow, prismatic needles melting at 183° (Found : N = 12·10. $C_{16}H_{15}O_2N_3Cl_2$ requires N = 11·94 per cent.).

III. m-4-*Xylyl* n-*Propyl Ketone* (XVI).

The following method of preparation gave a better yield of the ketone than that obtained by previous workers (Claus, *J. pr. Chem.*, 1891, [ii], **43**, 532; Klages, *Ber.*, 1902, **35**, 2257).

A small quantity of *n*-butyryl chloride was added to a mixture of *m*-xylene (34·6 grams) and aluminium chloride (27 grams). After the mixture had been warmed to 60° and an evolution of hydrogen chloride had commenced, further amounts of the acyl chloride were gradually added, the temperature being maintained at 50—60°. When all the *n*-butyryl chloride, amounting to 21·7 grams, had been added, the reaction was allowed to proceed at 50—60° with constant agitation for three hours, then at the ordinary temperature for a period of twelve hours and finally at 60° for three hours. The product, after being poured into water and washed with dilute sodium hydroxide solution, was dried and fractionally distilled. A fraction amounting to 26·25 grams was collected between 252° and 259°, and on repeated fractionation 23 grams of pure *m*-4-xylyl *n*-propyl ketone were obtained boiling at 258—259°/760 mm.; 9·95 grams of *m*-xylene were recovered, the yield of pure ketone amounting to 64 per cent. of the theoretical. *m*-4-Xylyl *n*-propyl ketone gave a p-*nitrophenylhydrazone*, which separated from alcohol in small, bright yellow crystals melting at 102—103° (Found : N = 13·79. $C_{18}H_{21}O_2N_3$ requires N = 13·50 per cent.).

6-*Nitro*-m-4-*xylyl* n-*Propyl Ketone* (XVII).—The introduction of one nitro-group into *m*-4-xylyl *n*-propyl ketone was effected by dissolving the ketone (8·8 grams) in twelve times its weight of concentrated sulphuric acid and, after cooling to 0°, adding slowly a mixture of 4·5 grams of nitric acid (*d* 1·42) and 36 grams of concentrated sulphuric acid. During the nitration the temperature was kept below 15° and the mixture stirred continuously for about two hours after all the nitric acid had been added. It was then poured on to crushed ice. The precipitated, semi-solid product was removed, and after it had been cooled to —10° and filtered at a low temperature there remained an almost white solid, which was washed successively with dilute sodium carbonate solution and water. It crystallised from warm alcohol in masses of slender, bayonet-shaped needles melting at 59—60° (Found: C = 65·2; H = 6·66; N = 6·43. $C_{12}H_{15}O_3N$ requires C = 65·13; H = 6·83; N = 6·33 per cent.).

6-*Nitro*-m-4-*xylyl* n-*propyl ketone* was only moderately soluble in cold alcohol, but more readily so in chloroform, light petroleum, or glacial acetic acid. On oxidation with an aqueous solution of chromic acid in presence of dilute sulphuric acid, 5-nitro-2 : 4-dimethylbenzoic acid was obtained, melting at 194—195° (Claus, *J. pr. Chem.*, 1890, [ii], **41**, 495, gives m. p. 195° [uncorr.]; Ahrens, *Annalen*, 1892, **271**, 18, gives m. p. 196—197°).

2-*Nitro*-m-4-*xylyl* n-*Propyl Ketone* (XIX).—The liquid product of the nitration, after being washed with sodium carbonate solution and water, deposited appreciable amounts of the 6-nitro-compound when cooled to —15°, and further quantities of the solid isomeride were removed by extracting the oily portion with small quantities of alcohol. After a prolonged treatment with alcohol at temperatures below 0°, an oil was obtained which did not solidify at —15° (Found: N = 6·42. $C_{12}H_{15}O_3N$ requires N = 6·33 per cent.). The oil, however, was not pure, for on oxidation a mixture of nitrodimethylbenzoic acids was obtained.

6-*Amino*-m-4-*xylyl* n-*propyl ketone* (XVIII), obtained by the reduction of the nitro-compound with zinc dust and ammonium chloride in alcoholic solution, separated from warm light petroleum in hard, almost colourless, hexagonal prismatic needles melting at 56° (Found: N = 7·44. $C_{12}H_{17}ON$ requires N = 7·33 per cent.). The *hydrochloride* crystallised from warm dilute hydrochloric acid in white, slender, acicular crystals (Found: Cl = 15·61. $C_{12}H_{17}ON,HCl$ requires Cl = 15·58 per cent.). The *sulphate* separated from water in long, fern-like crystals.

Acetylation with acetic anhydride yielded 6-*acetylamino*-m-4-*xylyl* n-*propyl ketone*, crystallising from petroleum (b. p. 80—100°) in a white, tangled mass of needles melting at 123° (Found: N = 6·35. $C_{14}H_{19}O_2N$ requires N = 6·01 per cent.). This amine, diazotised in dilute hydrochloric acid and coupled with alkaline β-naphthol, gave *butyro*-2 : 4-*dimethylphenone*-5-*azo*-β-*naphthol*, which crystallised from warm glacial acetic acid in bright red masses of slender needles and had a faint, green reflex (m. p. 194—195°) (Found: N = 8·44. $C_{22}H_{22}O_2N_2$ requires N = 8·09 per cent.). The azo-derivative was sparingly soluble in cold alcohol or glacial acetic acid, but dissolved more readily in chloroform; it dissolved in concentrated sulphuric acid to a reddish-purple solution.

6-*Chloro*-m-4-*xylyl* n-*Propyl Ketone* (XXI).—The replacement of the amino-group by chlorine was effected by the Sandmeyer reaction. This chloro-derivative was obtained by distillation in steam as an almost colourless oil, solidifying on cooling to 0°. Two crystallisations from alcohol at temperatures below 0° furnished a white, crystalline powder melting at 9—10° (Found: Cl = 16·44. $C_{12}H_{15}OCl$ requires Cl = 16·83 per cent.). This substance had a characteristic odour similar to that of honey, but not so powerful as that of 4-chlorophenyl *n*-propyl ketone.

Oxidation with chromic acid solution gave an acid which crystallised from alcohol in small, white needles melting at 165° after one crystallisation. This acid is presumably 5-*chloro*-2 : 4-*dimethylbenzoic acid*, which does not appear to have been previously described.

2 : 6-*Dinitro*-m-4-*xylyl* n-*Propyl Ketone* (XX).—*m*-4-Xylyl *n*-propyl ketone (1 gram) was nitrated by adding its solution in 9 grams of concentrated sulphuric acid to a mixture of 10·5 grams of nitric acid (*d* 1·5; free from nitrous acid) and 27 grams of sulphuric acid, cooled to —12°, and stirred continuously. On pouring on to ice, a milky, semi-solid mass separated, which was taken up with ether and washed successively with sodium carbonate solution, dilute sodium hydroxide, and water. Evaporation of the solvent gave 2 : 6-*dinitro*-m-4-*xylyl* n-*propyl ketone* as a pale yellow oil which solidified after two or three weeks; it separated from alcohol in a mass of white, hair-like needles melting at 63° (Found: N = 10·78. $C_{12}H_{14}O_5N_2$ requires N = 10·52 per cent.).

IV. p-*Dibutylbenzene* (XXII).

p-*Di*-n-*butylbenzene* was prepared by the action of sodium on a mixture of *p*-dichlorobenzene and *n*-butyl chloride. The yield, however, was small, and the numerous by-products obtained added to the difficulty of isolating the hydrocarbon in a pure state.

The reaction was carried out in a capacious flask immersed in an oil-bath, heated to 110° and subsequently to 150°. *n*-Butyl chloride (72 grams) and *p*-dichlorobenzene (60 grams) dissolved in 50 c.c. of xylene were gradually added to 50 grams of sodium shavings covered with xylene (75 c.c.), so that the heat of the reaction was just sufficient to keep the solvent boiling. The product was filtered to remove sodium and sodium chloride, and the cake of mineral matter was extracted thoroughly with warm benzene. After the bulk of the solvent had been removed from the combined extract and washings, a dark brown, viscous residue remained, having a faintly green appearance in reflected light. The product was distilled, fractions being collected up to 280—300°. By means of a lengthy process of fractionation, followed by treatment with metallic sodium, p-*di*-n-*butylbenzene* was obtained boiling at 224—225·5°/759 mm. (Found: C = 88·75, 88·76; H = 10·95, 11·30. $C_{14}H_{22}$ requires C = 88·34; H = 11·66 per cent.). After further distillations, the hydrocarbon gave C = 88·65; H = 11·3 per cent. Appreciable quantities of diphenyl were obtained in the reaction, and no doubt the presence of traces of diphenyl accounts for the high carbon content of the hydrocarbon. p-*Di*-n-*butylbenzene* is a colourless liquid having a faint, agreeable, orange-like odour.

2-*Nitro*-1 : 4-*di*-n-*butylbenzene*.—Dibutylbenzene (7 grams) was cooled to 0° and fuming nitric acid added in small quantities until 20 grams had been used. At the commencement of the operation the acid layer became dark red. The hydrocarbon on the other hand darkened as the nitration proceeded, until it was almost indistinguishable from the lower stratum. The nitration was checked as soon as nitrous fumes were evolved and the upper layer became lighter in colour. The crude nitro-compound was separated and treated repeatedly with water and sodium hydroxide solution until the washings were not tinted red. It was purified by distillation in steam, when 2-*nitro*-1 : 4-*di*-n-*butylbenzene* was obtained as a pale yellow, refractive liquid, having a pleasant and characteristic odour, faintly resembling that of lemons. It was purified for analysis by further distillation in steam, the first and the last portions of the distillate being rejected (Found: N = 6·14. $C_{14}H_{21}O_2N$ requires N = 5·95 per cent.).

2-*Amino*-1 : 4-*di*-n-*butylbenzene* (XXIII).—The reduction of 2-nitro-1 : 4-dibutylbenzene to the corresponding amino-compound did not proceed smoothly when zinc dust and ammonium chloride, or tin or zinc with aqueous or alcoholic hydrochloric acid were employed as reducing agents. More favourable results were obtained by the use of iron filings and acetic acid, but even under these conditions the product was contaminated with appreciable quantities of a less basic substance.

The nitro-compound (6·4 grams), dissolved in 15 c.c. of glacial acetic acid, was gradually added to 15 grams of iron filings covered with 50 grams of 80 per cent. acetic acid. The mixture was gently heated during the addition of the nitrodibutylbenzene and for a period of one hour after all the nitro-compound had been added. The bulk of the acetic acid was removed by distillation, and the crude amine isolated by distillation in steam after making the residue alkaline. It was partly purified by conversion into the sparingly soluble *sulphate*, which was extracted with ether. From the sulphate a moderately pure specimen of the base was obtained as a colourless liquid having a faint yet characteristic odour somewhat resembling that of mushrooms. The *hydrochloride*, which is soluble in water or chloroform, separated from dilute hydrochloric acid in white, flattened needles.

2-*Benzoylamino*-1 : 4-*di*-n-*butylbenzene*, after repeated crystallisation from alcohol, separated in white masses of needles melting at 116° (Found: C = 81·4; H = 8·6. $C_{21}H_{27}ON$ requires C = 81·5; H = 8·8 per cent.).

We desire to express our thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant which has partly defrayed the expense of this investigation.

THE CHEMICAL DEPARTMENT,
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CCXVII.—*The Nitro- and Amino-derivatives of 4-Phenylglyoxaline.*

By REGINALD LINDSAY GRANT and FRANK LEE PYMAN.

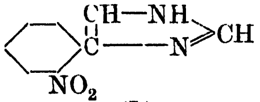
THE laws of substitution in the glyoxaline nucleus, and the properties conferred by it upon substituents in the 2- and 4- (or 5-) positions have been the subjects of previous papers by one of us and Dr. R. G. Fargher, and are being further investigated in these laboratories. The present work was carried out with the object of contributing to our present scanty knowledge of the somewhat unstable 4-aminoglyoxalines. The simplest member of the series is unknown, and the only substance which is known certainly to belong to this class is 4-amino-5-methylglyoxaline (Fargher, T., 1920, **117**, 668), although the same author (*loc. cit.*) has shown that the reduction product of 4-*p*-bromobenzeneazo-2-phenylglyoxaline (Fargher and Pyman, T., 1919, **115**, 258) is probably 5-amino-4-(5′-bromo-2′-aminophenyl)-2-phenylglyoxaline.

It was thought that a 4-amino-derivative of a 5-phenyl (or substituted phenyl)-glyoxaline might be stable and consequently 4-phenylglyoxaline was chosen as the starting material. This substance has been prepared previously by Pinner (*Ber.*, 1902, **35**,

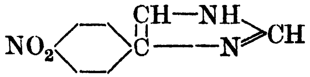
4131) by the action of ammonia on phenylglyoxal, but is more conveniently prepared by the application of Gabriel's method (*Ber.*, 1894, **27**, 1037) for the synthesis of glyoxalines, a method which has been employed for the synthesis of derivatives of 4-phenylglyoxaline, substituted in the benzene nucleus, by Stephen and Weizmann (T., 1914, **105**, 1046).

The interaction of ω-aminoacetophenone hydrochloride and potassium thiocyanate leads through *ω-aminoacetophenone thiocyanate* to *2-thiol-4-phenylglyoxaline*, which readily gives 4-phenylglyoxaline on oxidation.

Nitration of this substance, conveniently effected by dissolving its nitrate in sulphuric acid and heating the solution, yields a mixture of two mononitro-derivatives, which give on oxidation *o*- and *p*-nitrobenzoic acids respectively and are therefore *4-o- and 4-p-nitrophenylglyoxalines* (I and II).

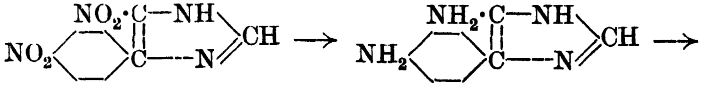


(I.)

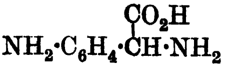


(II.)

Further nitration of 4-*p*-nitrophenylglyoxaline by the same method effects the introduction of a nitro-group into the glyoxaline nucleus, for the dinitrophenylglyoxaline obtained in this way yields *p*-nitrobenzoic acid almost quantitatively on oxidation. The fact that glyoxalines can be nitrated in the 4- (or 5-) but not in the 2-position indicates that this substance is 5-nitro-4-*p*-nitrophenylglyoxaline (III) and confirmation of this view was obtained by the complete reduction of the substance, when a diamino-4-phenylglyoxaline resulted which was not identical with 2-amino-4-*p*-aminophenylglyoxaline (Fargher and Pyman, *loc. cit.*), and was consequently 5-amino-4-*p*-aminophenylglyoxaline (IV). The dihydrochloride of this base is stable in aqueous solution, but undergoes decomposition when heated with hydrochloric acid at 170°, yielding ammonia and *p-aminophenylaminoacetic acid* (V).



(III.) (IV.)

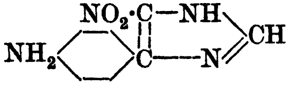


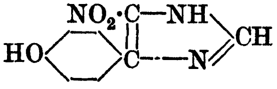
$$NH_2{\cdot}C_6H_4{\cdot}\overset{CO_2H}{C}H{\cdot}NH_2$$

(V.)

A further study of the preparation and properties of the diamine is contemplated.

Partial reduction of 5-nitro-4-*p*-nitrophenylglyoxaline by means of alcoholic ammonium sulphide led to the isolation of *5-nitro-4-*p*-aminophenylglyoxaline* (VI), the constitution of which follows from the facts (1) that its *acetyl* derivative gave a small quantity of *p*-acetylaminobenzoic acid on oxidation; (2) that it was unaffected by concentrated hydrochloric acid at 170°, unlike the diamine. Replacement of the amino-group of this substance by the hydroxy-group gave *5-nitro-4-*p*-hydroxyphenylglyoxaline* (VII).


(VI.)


(VII.)

In the course of this work, it was found that 4-phenylglyoxaline and its mononitro-derivatives gave the corresponding *N*-benzoyl derivatives when submitted to benzoylation by the Schotten-Baumann method, whereas in all previous applications of this method of benzoylation to glyoxalines, either derivatives of dibenzoylaminoethylene have been obtained, as in the case of glyoxaline itself (Bamberger and Berlé, *Annalen*, 1892, **273**, 342) and 4-methylglyoxaline (Windaus and Knoop, *Ber.*, 1905, **38**, 1166), or the substance has been recovered unchanged (Windaus, *Ber.*, 1909, **42**, 758; 1910, **43**, 499).

EXPERIMENTAL.

2-*Thiol-4-phenylglyoxaline.*

Concentrated aqueous solutions containing 30 grams of ω-aminoacetophenone hydrochloride and 17 grams of potassium thiocyanate respectively were mixed, and the liquor (L) evaporated to dryness on a water-bath. The residue was extracted with water, when 24·5 grams of crude 2-thiol-4-phenylglyoxaline remained in the form of small reddish-brown plates, melting at 254°. The yield thus amounts to 79 per cent. of the theoretical. After recrystallisation from alcohol (with the aid of animal charcoal), the substance was obtained in colourless plates, melting at 261° (corr.) (Found: C = 61·5, 61·4; H = 4·8, 4·5; N = 15·8, 15·7. $C_9H_8N_2S$ requires C = 61·3; H = 4·6; N = 15·9 per cent.). It is very sparingly soluble in cold water, readily soluble in acetone or alcohol, less readily so in ether, and very sparingly soluble in chloroform or benzene.

It is soluble in concentrated hydrochloric acid, forming a *hydrochloride*, which crystallises in clear prisms melting at 252° (corr.) and dissociates on the addition of water. It is soluble in dilute aqueous ammonia or sodium hydroxide, but not in cold aqueous sodium carbonate. It gives a cherry-red colour with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

The *picrate* is obtained in garnet-red, hexagonal tablets, melting at 182° (corr.), on mixing molecular proportions of the constituents in concentrated absolute alcoholic solution. When dissolved in hot water, it dissociates into its components.

An intermediate product in the preparation of 2-thiol-4-phenylglyoxaline can be isolated by concentrating the liquor (L) to a small volume under diminished pressure, when on cooling *ω-aminoacetophenone thiocyanate* separates in long, colourless needles, melting at 135° (corr.) (Found: $C = 55{\cdot}5$, $55{\cdot}6$; $H = 5{\cdot}3$, $5{\cdot}2$; $N = 14{\cdot}2$, $14{\cdot}2$. $C_9H_{10}ON_2S$ requires $C = 55{\cdot}6$; $H = 5{\cdot}2$; $N = 14{\cdot}4$ per cent.). It is readily soluble in water, and is unstable, being readily converted into 2-thiol-4-phenylglyoxaline by heating at 100°. The possibility that this compound was the isomeric thiocarbamide is eliminated by the fact that it gives a deep red colour with ferric chloride, and can be readily converted into ω-aminoacetophenone picrate, which melts at 174° (corr.).

4-*Phenylglyoxaline.*

Twenty-four grams of crude 2-thiol-4-phenylglyoxaline (m. p. 254°) were added slowly to 480 c.c. of gently boiling 10 per cent. nitric acid. After being boiled for another fifteen minutes, the liquor was kept and deposited 25 grams of crude 4-phenylglyoxaline nitrate melting at 170°, that is, 88 per cent. of the theoretical yield.

This *nitrate* separates from water in long, pale yellow, prismatic needles, which melt at 179° (corr.). It is soluble in about 8 parts of boiling water, is feebly acid to litmus, and is anhydrous (Found: $N = 20{\cdot}4$, $20{\cdot}3$. $C_9H_8N_2,HNO_3$ requires $N = 20{\cdot}3$ per cent.). The corresponding base was found to melt at 128° (corr.); Pinner (*loc. cit.*) gives 128—129°.

The *hydrochloride* forms long, colourless needles, which melt at 180° (corr.) and are very readily soluble in water. The *hydrogen oxalate* crystallises from water in broad needles, which melt at 199° (corr.), and are only moderately readily soluble in cold water. The *picrate* forms long, yellow needles, which melt at 216° (corr.), and are soluble in about 140 parts of hot water.

4-Phenylglyoxaline gives a deep cherry-red colour with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

Nitration of 4-Phenylglyoxaline. Isolation of 4-o- *and* 4-p-*Nitrophenylglyoxalines.*

Twenty grams of 4-phenylglyoxaline nitrate were added to 40 c.c. of sulphuric acid, the temperature of the mixture being kept below 30°. The product was heated under reflux for two hours on a water-bath, then diluted with 400 c.c. of water, heated to about 60°, and neutralised by the addition of, first, sodium hydroxide, then sodium carbonate. From the hot solution, 16·8 grams of crude 4-*p*-nitrophenylglyoxaline, melting at 218°, separated, whilst the filtrate on cooling deposited 1·7 grams of the crude *ortho*-isomeride, melting at 134°, a further small quantity of this being obtained on concentrating the liquor. The various crops were converted into the nitrates and fractionated, the bases being then regenerated from the salts and recrystallised. In the case of the *ortho*-compound, crystallisation of the hydrochloride also was effective. By these means, there were isolated in a pure state 12·7 grams of 4-*p*-nitrophenylglyoxaline and 4·6 grams of 4-*o*-nitrophenylglyoxaline, the yields amounting to 69 and 25 per cent. of the theoretical respectively.

4-o-*Nitrophenylglyoxaline* crystallises from alcohol in pale yellow, elongated, glistening plates, which melt at 146° (corr.). In the dry state this base (but not its salts) rapidly turns green under the influence of light, and in strong sunlight becomes dark olive-green in the course of half an hour. It is insoluble in cold, but sparingly soluble in hot, water, very readily soluble in alcohol or acetone, soluble in ether or chloroform, and sparingly soluble in benzene or light petroleum (Found: C = 57·1, 57·0; H = 3·9, 3·7; N = 22·3, 22·3. $C_9H_7O_2N_3$ requires C = 57·1; H = 3·7; N = 22·2 per cent.).

It is readily soluble in dilute mineral acids giving colourless solutions, and in caustic alkalis giving yellow to deep orange solutions. It gives a cherry-red colour with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

The *hydrochloride* crystallises from water in large, clear greenish yellow prisms which melt at 203° (corr.) and are anhydrous. It is very easily soluble in water, giving a strongly acid solution (Found: Cl = 15·5, 15·6. $C_9H_7O_2N_3$, HCl requires Cl = 15·7 per cent.).

The *nitrate* crystallises from water, in which it is easily soluble, in pale yellow needles, which decompose at about 168° (corr.), and are anhydrous (Found: N = 22·2. $C_9H_7O_2N_3,HNO_3$ requires N = 22·2 per cent.).

4-p-*Nitrophenylglyoxaline* crystallises from alcohol in canary-yellow needles, which melt at 225° (corr.). It is insoluble in water, even hot, readily soluble in alcohol or acetone, sparingly soluble in ether or chloroform, and only very sparingly so in benzene or light petroleum (Found: C = 56·9, 57·0; H = 3·9, 3·7; N = 22·2, 22·2. $C_9H_7O_2N_3$ requires C = 57·1; H = 3·7; N = 22·2 per cent.).

It is readily soluble in dilute mineral acids giving colourless solutions, and in caustic alkalis giving yellow to deep orange solutions. It gives a cherry-red colour with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

The *hydrochloride* forms very pale buff needles from alcohol. It melts at 292° (corr.) and is anhydrous. It is very easily soluble in water giving a strongly acid solution, and easily soluble in hot alcohol (Found: C = 47·7; H = 3·6; N = 18·6, 18·7; Cl = 15·7. $C_9H_7O_2N_3,HCl$ requires C = 47·9; H = 3·6; N = 18·6; Cl = 15·7 per cent.).

The *nitrate* crystallises from water in pale yellow needles, which melt at 200° (corr.). It is soluble in about 25 parts of boiling water and is anhydrous (Found: N = 22·2. $C_9H_7O_2N_3,HNO_3$ requires N = 22·2 per cent.).

Nitration of 4-p-*Nitrophenylglyoxaline. Isolation of* 5-*Nitro*-4-p-*nitrophenylglyoxaline.*

Twenty grams of 4-*p*-nitrophenylglyoxaline nitrate were added to 40 c.c. of sulphuric acid, and the mixture was heated under reflux for two hours on a water-bath. After cooling, the mixture was diluted with 400 c.c of water, when a cream-coloured precipitate was obtained. This was extracted with hot dilute hydrochloric acid and left 17·2 grams of the nearly pure dinitro-compound, whilst 0·9 gram of pure 4-*p*-nitrophenylglyoxaline was isolated from the mother-liquors. The yield, allowing for the recovered material, is almost quantitative.

5-*Nitro*-4-p-*nitrophenylglyoxaline* crystallises from alcohol in colourless needles which melt at 293° (corr.). It is insoluble in cold and very sparingly soluble in boiling water, fairly easily soluble in alcohol or acetone, sparingly soluble in ether, and very sparingly so in chloroform (Found: C = 46·0, 46·1; H = 2·6, 2·6; N = 24·0, 24·1. $C_9H_6O_4N_4$ requires C = 46·1; H = 2·6; N = 23·9 per cent.).

It is soluble in strong mineral acids, but is precipitated unchanged on the addition of water; it dissolves in dilute aqueous ammonia, sodium carbonate, or sodium hydroxide, giving yellow solutions. The sodium, potassium, and ammonium salts form pale yellow needles and are sparingly soluble in cold water. It gives no coloration with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

The *nitrate* crystallises from 50 per cent. nitric acid in large, flat needles. It dissociates on treatment with water, or when heated at 100°, the residue consisting of the base (Found: loss at 100° = 21·2. $C_9H_6O_4N_4,HNO_3$ requires loss of HNO_3 = 21·2 per cent.).

Benzoylation of 4-*Phenylglyoxaline and its Nitro-derivatives.*

When treated with benzoyl chloride and aqueous sodium hydroxide at the laboratory temperature, 4-phenylglyoxaline and its *o*- and *p*-nitro-derivatives gave benzoyl derivatives, which, after washing with a little ether, were obtained in yields of 90—97 per cent. of the theoretical, the crude products melting at 120°, 97°, and 176° respectively. After recrystallisation from alcohol, the products were as follows:

1-*Benzoyl*-4 (or 5)-*phenylglyoxaline* (*A*).—Colourless needles melting at 132° (corr.) (Found: C = 77·2, 77·4; H = 4·8, 4·9; N = 11·1, 11·2. $C_{16}H_{12}ON_2$ requires C = 77·4; H = 4·9; N = 11·3 per cent.).

1-*Benzoyl*-4 (or 5)-o-*nitrophenylglyoxaline* (*B*).—Elongated plates, which melt at 100—101° (corr.) (Found: C = 65·4, 65·4; H = 3·8, 3·7; N = 14·2, 14·2. $C_{16}H_{11}O_3N_3$ requires C = 65·5; H = 3·8; N = 14·3 per cent.).

1-*Benzoyl*-4 (or 5)-p-*nitrophenylglyoxaline* (*C*).—Pale yellow, flat needles, melting at 182° (corr.) (Found: C = 65·5, 65·4; H = 3·9, 3·8; N = 14·2, 14·2. $C_{16}H_{11}O_3N_3$ requires C = 65·5; H = 3·8; N = 14·3 per cent.).

The three benzoyl derivatives are insoluble in water or dilute aqueous sodium hydroxide, easily soluble in hot alcohol, and sparingly soluble in ether. They differ in stability. A pure sample of *A*, kept for four weeks in a well-corked bottle, had become almost converted into an oil, from which 4-phenylglyoxaline and benzoic acid were isolated. Moreover, this substance can be recrystallised from alcohol only in small yield owing to hydrolysis. *B* and *C* are stable when pure, and *C* is decomposed to a much smaller extent than *A* on boiling with alcohol, whilst *B* scarcely suffers hydrolysis under these conditions. All three compounds are rapidly hydrolysed by hot dilute hydrochloric acid.

5-Nitro-4-*p*-nitrophenylglyoxaline was recovered unchanged after treatment with benzoyl chloride and aqueous sodium hydroxide.

Oxidation of the Nitro-derivatives of 4-Phenylglyoxaline.

The nitro-derivatives of 4-phenylglyoxaline (1/100 gram-mol.) were dissolved in 250 c.c. of boiling water containing one equivalent of potassium hydroxide, and oxidised with the calculated quantity (4·2 grams) of potassium permanganate. Under these conditions 4-*p*-nitrophenylglyoxaline and 5-nitro-4-*p*-nitrophenylglyoxaline each gave *p*-nitrobenzoic acid in almost quantitative yield; the crude acid (of which the main crops melted at 232° and 226° in the two cases) amounted to 1·65 grams in each case and readily gave the pure acid, which melted at 237° (corr.), alone and when mixed with a reference specimen. 4-*o*-Nitrophenylglyoxaline under the same conditions gave an oily acid which reduced permanganate, and on further treatment with this reagent gave *o*-nitrobenzoic acid, melting at 147° (corr.), alone or mixed with a reference specimen, in a yield of 45 per cent. of the theoretical.

5-*Amino*-4-p-*aminophenylglyoxaline.*

Seven grams of 5-nitro-4-*p*-nitrophenylglyoxaline were gradually added to a solution of 42 grams of hydrated stannous chloride in 105 c.c. of hydrochloric acid, the temperature being kept below 15°. The crystalline stannichloride, which separated on heating, was deprived of tin, when 2·8 grams of 5-amino-4-*p*-aminophenylglyoxaline dihydrochloride were obtained, that is, 37 per cent. of the theoretical yield.

5-*Amino*-4-p-*aminophenylglyoxaline dihydrochloride* crystallises from water in colourless, prismatic needles, which darken at about 260°, but do not melt at 300°. This salt is anhydrous, very easily soluble in water, and very sparingly so in absolute alcohol (Found: C = 43·6, 43·6; H = 5·1, 5·0; N = 22·5, 22·5; Cl = 28·8, 29·0. $C_9H_{10}N_4,2HCl$ requires C = 43·7; H = 4·9; N = 22·7; Cl = 28·7 per cent.). Aqueous solutions of the salt give (1) with alkalis, no precipitate, but slowly become oxidised in the air, turning pink and then purple; (2) with nitrous acid, a yellow solution which gives with aqueous sodium hydroxide a clear purple-red solution, and with aqueous sodium β-naphthoxide a sparingly soluble, purple precipitate; (3) with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate, a deep reddish-brown solution; (4) with sodium nitroprusside, no colour, but on subsequent addition of sodium hydroxide, an intense dull-brown solution; (5) with sodium acetate and benzaldehyde, a yellow, crystalline benzylidene derivative; (6) with picric acid, a picrate, which crystallises from water in greenish-yellow needles and does not melt at 300°; (7) with sulphuric acid, a very sparingly soluble sulphate forming colourless, glistening needles.

Action of Hydrochloric Acid at 170°.—One gram of the diamine dihydrochloride and 10 c.c of concentrated hydrochloric acid were heated for three hours at 170°. The product consisted of 0·7 gram of colourless crystals and a mother-liquor which gave a residue of 0·6 gram, largely ammonium chloride. The mode of formation and the properties of the former substance indicate that it is p-*aminophenylaminoacetic acid dihydrochloride.* It was recrystallised from dilute hydrochloric acid and formed colourless, prismatic needles which did not melt at 280°, and were anhydrous (Found: Cl = 29·9. $C_8H_{10}O_2N_2,2HCl$ requires Cl = 29·7 per cent.). It was easily soluble in water and strongly acid. After diazotisation, it coupled with β-naphthol. When mixed with sodium acetate in concentrated aqueous solution until no longer acid to methyl-orange, the sparingly soluble *monohydrochloride* separated in colourless, glistening plates which had no sharp melting point, but began to turn brown at about 200° and were completely decomposed at 250° (Found: C = 47·4; H = 5·4; N = 13·8. $C_8H_{10}O_2N_2,HCl$ requires C = 47·2; H = 5·5; N = 13·7 per cent.).

5-*Nitro*-4-p-*aminophenylglyoxaline.*

Five grams of 5-nitro-4-*p*-nitrophenylglyoxaline were dissolved in 700 c.c of alcohol and 25 c.c. of aqueous ammonia (*d* 0·880), and hydrogen sulphide was passed through the solution for two hours. The solution was then boiled under reflux for half an hour and kept. The red precipitate was collected, and extracted with 10 per cent. aqueous hydrochloric acid, which removed 3·2 grams of nitroaminophenylglyoxaline dihydrochloride, that is, 53 per cent. of the theoretical yield.

5-*Nitro*-4-p-*aminophenylglyoxaline dihydrochloride* crystallises from dilute hydrochloric acid in yellow, prismatic needles, which turn red at about 220° and decompose at about 250° (corr.) (Found: C = 38·9, 38·9; H = 3·8, 3·6; N = 20·2, 20·2; Cl = 25·3, 25·4. $C_9H_8O_2N_4,2HCl$ requires C = 39·0; H = 3·6; N = 20·2; Cl = 25·6 per cent.). It is easily soluble in dilute hydrochloric acid, but dissociates on the addition of water, yielding the base as a bright terracotta precipitate, almost insoluble in water or the usual organic solvents, even when hot (Found: in base dried at 100°, C = 52·8, 52·6; H = 3·9, 3·8; N = 27·3, 27·3. $C_9H_8O_2N_4$ requires C = 52·9; H = 4·0; N = 27·5 per cent.). This is soluble in sodium hydroxide or ammonia (but not in sodium carbonate), giving yellow to red solutions; the sodium salt crystallises from water in red needles.

Solutions of the hydrochloride in dilute hydrochloric acid give (1) no change in colour on the addition of sodium nitrite, but on adding this solution to aqueous sodium hydroxide, a deeper yellow colour, and on adding it to aqueous sodium β-naphthoxide, a reddish-brown solution, (2) on the addition of aqueous sodium hydroxide, a reddish-brown colour with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

The dihydrochloride is recovered unchanged after heating with 10 parts of concentrated hydrochloric acid for two and a half hours at 170°.

*5-Nitro-*p*-acetylaminophenylglyoxaline*, prepared by heating the above dihydrochloride with acetic anhydride and sodium acetate, forms a bright yellow powder, which does not melt at 280°, and is almost insoluble in water and the usual organic solvents, even when hot. It dissolves in concentrated hydrochloric acid, but is reprecipitated on diluting the solution. It is soluble in aqueous ammonia, sodium carbonate, or hydroxide (Found: in substance dried at 100°, $C = 53{\cdot}5$, $53{\cdot}6$; $H = 4{\cdot}4$, $4{\cdot}2$; $N = 22{\cdot}7$, $22{\cdot}6$. $C_{11}H_{10}O_3N_4$ requires $C = 53{\cdot}6$; $H = 4{\cdot}1$; $N = 22{\cdot}8$ per cent.).

Oxidation.—2·46 Grams of the acetyl derivative were dissolved in a solution of 0·56 gram of potassium hydroxide in 100 c.c. of water mixed with a solution of 4·2 grams of potassium permanganate in 105 c.c. of water, and heated for three-quarters of an hour on the water-bath. The manganese hydroxide having been removed, the liquor was acidified with hydrochloric acid, filtered from 0·3 gram of apparently unchanged acetyl derivative, and extracted with ether. The ethereal extract was evaporated and gave 0·1 gram of crude *p*-acetylaminobenzoic acid, melting at 240°. After purification, a small amount of the pure acid was obtained melting at 260° (corr.), alone or when mixed with a specimen of the pure acid from another source. The identification was confirmed by hydrolysis to *p*-aminobenzoic acid, which melted at 190° (corr.), alone or mixed with a specimen of the pure acid from another source.

*5-Nitro-4-*p*-hydroxyphenylglyoxaline* separates as a sandy powder in good yield when 5-nitro-4-*p*-aminophenylglyoxaline dissolved in excess of 20 per cent. aqueous sulphuric acid is treated with the equivalent quantity of sodium nitrite, at the ordinary temperature, and the solution is heated and kept. It crystallises from about 1000 parts of boiling water in golden, feathery needles which do not melt at 300°. It is soluble in moderately concentrated acids when hot, and yields a crystalline hydrochloride with concentrated hydrochloric acid. It is soluble in alkalis, even in sodium carbonate, with a deep red colour (Found: N = 19·9. $C_9H_7O_3N_3$ requires N = 20·5 per cent.).

We are indebted to Miss Esther Levin, M.Sc. Tech., for several analyses carried out in connexion with this investigation.

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CCXVIII.—*The Explosion of Acetylene and Nitrogen. Part I.*

By William Edward Garner and Kichimatsu Matsuno.

The observations of Berthelot form the basis of almost every investigation into the phenomena of explosive processes, and it is thus not surprising that the reaction between acetylene and nitrogen was first studied by this great chemist. Berthelot showed that endothermic substances like acetylene, cyanogen, arsenic trihydride, and nitric oxide were readily detonated at atmospheric pressure by means of a fulminate detonator. The detonation could not, however, be brought about by an electric spark, in the case of acetylene, unless the pressure exceeded two atmospheres. A partial decomposition of the acetylene into carbon and hydrogen occurred during sparking, but the heat of decomposition was not liberated sufficiently quickly to start the explosion wave.

When acetylene and nitrogen are sparked at atmospheric pressure, carbon and hydrocyanic acid are produced (Berthelot, *Compt. rend.*, 1868, **67**, 1141). The decomposition of carbon can, however, be avoided and the conversion of acetylene into hydrocyanic acid made quantitative, in the presence of an excess of hydrogen, if the acid is removed by alkali as soon as it is formed. A further study of this reaction was made by Mixter (*Amer. J. Sci.*, 1900, [iv], **9**, 1; 1900, [iv], **10**, 299), who exploded mixtures of acetylene and nitrogen in glass manometers and steel vessels. Both hydrocyanic acid and ammonia were found in the products of explosion. The primary reaction is probably the decomposition of acetylene into hydrogen and carbon, and this is followed by a reaction between the products and nitrogen. At the moment of explosion, among other substances, a mixture of carbon, hydrogen, and nitrogen is obtained, which reacts to give hydrocyanic acid and ammonia. The results of Wallis (*Annalen*, 1906, **345**, 356) and Wartenberg (*Zeitsch. anorg.*

Chem., 1907, 52, 299) on the equilibrium between carbon, hydrogen, and nitrogen will thus be of interest. In these experiments with an equimolecular mixture of hydrogen and nitrogen it was found that about 40 per cent. of hydrocyanic acid was produced at 3300° and 4 per cent. at 1830°.

In many modern explosives, the deficiency of oxygen is so large that carbon is one of the products of detonation. During the cooling of the gases by radiation and by the work done on the container, this carbon reacts with the nitrogen present in the explosive to give hydrocyanic acid. The percentage of this gas in the gaseous products may be quite large, as was shown by Berthelot and Veille in the case of the detonation of benzenediazonium nitrate; 3·2 per cent. of the total gases was hydrocyanic acid. Trinitrotoluene also gives large quantities of hydrocyanic acid on detonation.

The products of an explosive decomposition are very largely determined by the rate of cooling; the slower the rate of cooling of the gases the lower the temperature at which the "chilling" of the gaseous equilibria takes place. This is of special importance in the hydrocyanic acid equilibria in the gases from explosives, for during the cooling a portion of the carbon liberated at the higher temperatures disappears according to the reaction :

$$CO_2 + C = 2CO.$$

The presence of oxygen in the gases introduces a complication into the nitrogen equilibria, which makes their investigation difficult.

It was with the view of throwing light on these complex equilibria, occurring during cooling, that this investigation was undertaken. It was considered that the explosion of acetylene with nitrogen or of cyanogen with hydrogen would give rise to conditions which, while being similar to those occurring in the explosion of high explosives, would be free from the complications due to the presence of oxygen. The effect of the addition of oxygen to the mixture could then be studied.

EXPERIMENTAL.

(*a*) *Materials.*—The acetylene was obtained from a solution of this gas in acetone kindly supplied by Allen Liversidge, Ltd. Except for the presence of acetone, the gas was almost free from impurities; the first fraction gave 1—2 per cent. of hydrogen and nitrogen, but these constituents rapidly diminished to a negligible quantity as the acetylene was consumed. The percentage of acetylene in the gas liberated is calculated to be approximately 0·5 per cent. at a pressure in the cylinder of 20 atmospheres. It is thus possible that the gas contained 0·25 per cent. of oxygen, and since the larger portion of this will be burnt to carbon monoxide, the amount of water produced on explosion will be very small. This small quantity of water formed on explosion, however, makes the analysis more difficult, for a mixture of hydrocyanic acid and ammonia in the presence of moisture attacks mercury.

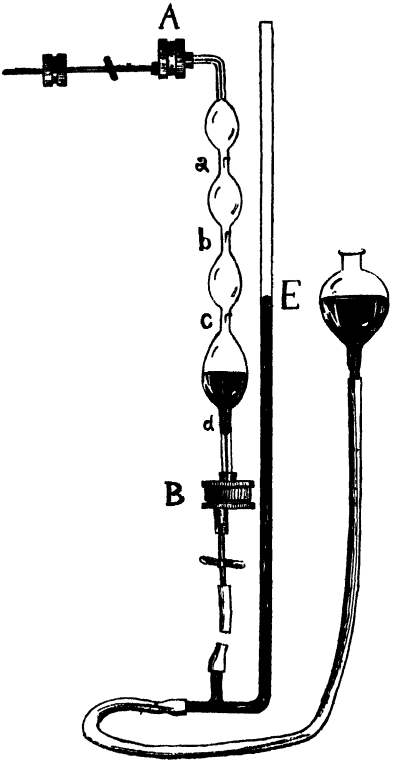
The nitrogen was prepared from ammonium sulphate and sodium nitrite in aqueous solution in the presence of potassium dichromate (Veley, T., 1903, **83**, 736); in addition, a little litharge was added. The nitrogen was stored over a suspension of ferrous hydroxide in water to remove nitric acid and to prevent the entrance of oxygen from the air, and was finally dried over phosphoric oxide. The mixtures of nitrogen and acetylene were analysed in a constant-volume apparatus.

(*b*) *Bomb.*—Preliminary experiments showed that dry hydrocyanic acid and ammonia were without action on the metals employed in the construction of pressure vessels, and there appeared to be no objection to the use of phosphor-bronze as a bomb material. A phosphor-bronze bomb, similar in design to that used by Wheeler (T., 1918, **113**, 855), but with 3/8 inch in thickness of walls and without the manometer, was obtained from Chas. Cook, the Manchester University Engineering Works. This was 3·988 litres in capacity and held a vacuum for twenty-four hours without appreciable leakage. A little vaselin was all that was necessary to make the joint gas-tight. It was found, however, that a loss of gas occurred at the large joint (annealed copper washer) at the moment of explosion, but as the joint held a vacuum after the experiment, this leakage was not a serious disadvantage.

(*c*) *Measurement of Pressures.*—Before the gas was introduced, the bomb was evacuated to a pressure of 1 mm. by means of a Cenco-Nelson oil-pump, and the pressure read off on a small McLeod gauge. The dry nitrogen was then introduced, and since the pressure did not reach 1 atmosphere, the measurement of this offered no difficulty. The acetylene was introduced directly into the bomb up to a pressure of 3·4 atmospheres, and after allowing time for the mixing of the gases, a sample was taken for analysis and the pressure measured accurately. For this purpose a new type of manometer was constructed, capable of reading up to five atmospheres. The principle adopted was to expand a known volume of the gas, at the pressure in the bomb, to approximately atmospheric pressure and to measure the new pressure on a mercury-glass manometer. A diagram of the manometer is given in Fig. 1, The apparatus consists of a series of glass bulbs *A* to *B* closed at both ends by two glass-to-metal taps *A* and *B* (*J. Soc. Chem. Ind.*, 1920, **39**, 247T) and attached to the manometer *E*. The volumes enclosed by mercury between the blue-glass tips *a*, *b*, *c*, and *d* and the tap *A*, were accurately determined.

Before the experiment, the apparatus is filled with mercury up to the tip *a*, and the tap *B* is closed. The gases from the bomb are then admitted into the first bulb, and the tap *A* is closed. Since in these experiments the pressure of the gas was 3—3·5 atmospheres, it was allowed to expand to the blue pointer, *c*, by opening the tap *B* and adjusting the level in *E*. The pressure was calculated from this level and the ratio of the volume of the bulbs. No correction was applied for the increase in volume in the first bulb, due to the compression of mercury and glass, since the order of accuracy required was less than 1 in 1000.

FIG. 1.



Explosion of Gases.

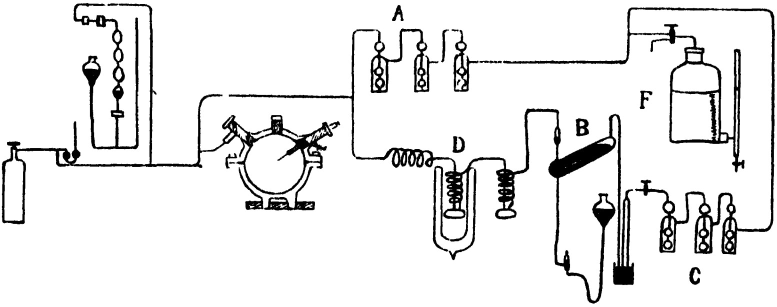
The explosive mixture was fired by the fusion of thin iron wire placed across the terminals in the centre of the bomb. Occasionally loss of gas occurred on explosion, which was detected by the smell of hydrocyanic acid. The joint, however, tightened up immediately and held a vacuum after the experiment. The bomb was distinctly warm to the hand after the explosion, and a marked difference in the temperature of the thin metal parts was observed in experiments on the explosion of pure acetylene and that of a mixture containing 20 per cent. of nitrogen.

This behaviour would be explained by different rates of burning of the acetylene and nitrogen mixture. In experiment XIV, with 14 per cent. of nitrogen, it is evident that the explosion was incomplete.

Analysis and Measurement of Volume of Gases.

On account of the loss of gas (0·5 per cent.), the volume of the gases was measured after the explosion. The gases were led through bubblers (*A*, Fig. 2) to remove hydrocyanic acid and ammonia, into a large aspirator, *F*, fitted with a water manometer. The pressure in the aspirator was maintained at atmospheric, throughout, and the volume of the gases was measured by a determination of the water displaced. The first litre of gas, containing air from the bubblers, was measured and rejected. The remainder of the gas was collected in the aspirator and a portion analysed as a check. Some acetylene dissolved in the water, and the percentage of this gas was therefore low. For comparison, a sample was taken directly from the bomb after the pressure had fallen to two atmospheres, and except for the slight difference due to the removal of a portion of acetylene in the first sample, the two analyses were in good agreement.

FIG. 2.



The gases in the bomb were dealt with in this way at pressures from three down to one atmosphere. From this point they were removed by means of a Toepler pump, *B*. On account of the small amount of water present, it was important to eliminate the hydrocyanic acid, ammonia, and water by means of liquid air, *D*, before passing the gases through the pump. The latter were collected at the base of the pump and transmitted through the bubblers, *C*, containing dilute acid and alkali, to the aspirator.

The total volume of the gases obtained in this manner, corrected for the vapour pressure of water and reduced to N.T.P., was used in calculating the percentages of ammonia and hydrocyanic acid.

The evacuation was carried out down to 2—3 mm., dry air admitted, and the bomb further evacuated. This was done as a precaution, but the quantities of hydrocyanic acid removed at this stage were negligible.

The gases condensed in *D* were evaporated into the bubblers, *A*, and the solutions in *C* added to the respective solutions in *A*. The amounts trapped in *C* were negligible, showing that the whole of the hydrocyanic acid had been removed by liquid air.

The connecting tubes were all glass except where joined to the metal tube from the bomb by a short length of rubber tubing.

Hydrocyanic Acid and Ammonia.

It was found that hydrocyanic acid could be estimated by distillation from 0·5 per cent. sulphuric acid solutions without appreciable hydrolysis. The gases could thus be absorbed in a series of bubblers, *A*, containing normal acid and dilute alkali. The acid solution containing hydrocyanic acid was then distilled into alkali and the whole of the hydrocyanic acid solutions were combined. The ammonia was estimated in the usual manner; the back-titration method gave the same result as the direct method. The hydrocyanic acid was estimated by (*a*) silver nitrate with potassium iodide as indicator (Denige, "Classen," Anal. Chem. p. 675), and (*b*) iodometrically (Fordos and Gélis, *J. Pharm. Chim.*, 1853, [iii], **23**, 48). The result obtained in (*a*) was usually 0·5 per cent. higher than that in (*b*); the mean value was taken.

The possibility of the loss of hydrocyanic acid by combination with the metal of the bomb must not be overlooked, but from the ease with which the results were reproduced (these are independent of the time the gases remain in the bomb) it appears that no appreciable action has occurred. Also, the interior of the bomb was as bright at the conclusion of these experiments as at the beginning. It was anticipated that the liquid hydrocyanic acid collected in the liquid-air tubes would show some tendency to polymerisation, but this was not found to be the case.

The carbon residue was analysed for hydrocyanic acid and ammonia, but these two gases were not present.

Permanent Gases.

The acetylene, hydrogen, and nitrogen in the residual gases were estimated in a constant-volume apparatus. Some difficulty was experienced in estimating the nitrogen with sufficient accuracy by the explosion method. In the later experiments, however, after the removal of the acetylene, the hydrogen was absorbed over copper oxide in a quartz tube, pure carbon dioxide being used to wash out the tube and to drive the gas into the measuring apparatus. The percentage of nitrogen was in good agreement with the calculated value (Table II). A little carbon monoxide could be detected in some of the experiments. Benzene and other condensed substances could only have been present in small amounts.

Discussion of Results.

The experimental data are given in Tables I and II, the Roman numerals indicating the order in which the experiments were performed. The results of all the experiments are given.

TABLE I.

No. of expt.	Initial temp.	Initial percentage of N.	Initial pressure in atm.	Final pressure in atm.	C.c. of HCN.	C.c. of NH_3.	Total volume of gases in c.c.
II	13°	2·97	3·21	3·05	(168·7)	(7·3)	12180
XIII	—	3·12	—	3·24	203·6	14·2	12940
I	15	3·15	3·22	3·05	(123·0)	(4·0)	12180
III	14	3·29	3·24	3·10	(188·9)	(8·0)	12400
XI	16	5·29	3·24	3·27	282·8	18·7	13090
VII	13·0	5·71	3·22	3·25	284·9	16·3	13000
V	10	9·66	3·26	3·16	340·1	16·8	—
VIII	14	9·71	3·33	3·29	356·0	17·7	13240
VI	12	10·44	3·26	3·33	362·7	20·6	13310
IV	12·5	12·06	3·20	3·19	371·4	—	12750
IX	14	12·88	—	3·09	360·3	18·3	12370
XIV	—	14·27	—	3·24	360·3	20·3	12950
X	15·5	18·04	3·26	3·10	381·0	20·5	12410
XII	18	22·05	3·01	2·95	388·2	16·9	12010

The first three experiments I, II, and III may be disregarded, as in these cases the methods of analysis had not been completely worked out. With two exceptions the pressures of the mixed gases lie between 3·21 and 3·26 atmospheres. It will be observed that the volume of the hydrocyanic acid increases with the quantity of nitrogen in the gases, whereas the ammonia is almost constant throughout. The volume of gases given in the last column of Table I includes the hydrocyanic acid and ammonia.

The carbon deposited in the bomb was removed, mixed with copper oxide, and heated in a stream of carbon dioxide, and the amount of nitrogen present was determined. The volume of the nitrogen which was fixed on the surface of the carbon was certainly less than 1 c.c., that is, less than 0·01 per cent. of the total gas.

Since the main chemical reactions, during the explosion and the cooling of the gases, are not accompanied by any change in the number of molecules of gas, the initial and the final pressures should be the same. The values in the fourth and the fifth columns

TABLE II.

Percentage Composition of the Residual Gases.

No. of expt.	N_2. Calc.	N_2. Obs.	H_2. Calc.	H_2. Obs.	HCN.	NH_3.	C_2H_2.
II	2·25	(2·39)	93·6	(93·4)	1·38	0·060	2·76
XIII	2·28	2·41	94·1	94·0	1·57	0·110	1·93
I	2·63	—	94·2	—	1·01	0·033	2·10
III	2·49	(2·77)	93·4	(93·1)	1·52	0·065	2·34
XI	4·13	4·34	91·2	91·0	2·17	0·143	2·48
VII	4·55	(4·67)	91·3	(91·2)	2·19	0·125	1·78
V	8·25	(8·55)	86·3	(86·0)	2·69	0·133	2·63
VIII	8·28	(8·43)*	86·8	86·7*	2·72	0·135	2·11
VI	9·00	(9·32)	85·8	(85·5)	2·73	0·154	2·29
IV	10·61	(10·81)	83·4	(83·7)	2·91	—	2·56
IX	11·34	(11·49)	83·5	(83·3)	2·92	0·148	2·12
XIV	12·80	12·46	78·7	79·0	2·78	0·157	5·53
X	16·42	—	78·1	—	3·07	0·165	2·24
XII	20·33	19·92	74·3	74·7	3·24	0·141	1·96

* Hydrogen estimated by the palladium method; the other values in brackets were obtained by the explosion method.

TABLE III.

No. of expt.	N_2 (Calc.)	$\frac{[NH_3]}{[HCN]}$.	$\frac{[NH_3]}{[H_2][HCN]}$.	$\frac{[HCN]^2}{[H_2][N_2]}$.	$\frac{[HCN]}{[H_2][N_2]^{0·3}}$.
XIII	2·28	0·070	0·00074	0·0115	0·0126
XI	4·13	0·066	0·00072	0·0125	0·0141
VII	4·55	0·057	0·00063	0·0116	0·0137
V	8·25	0·049	0·00057	0·0101	0·0142
VIII	8·28	0·050	0·00057	0·0103	0·0143
VI	9·00	0·057	0·00066	0·0097	0·0141
IV	10·61	—	—	0·0095	0·0145
IX	11·34	0·051	0·00061	0·0090	0·0143
XIV	12·80	0·057	0·00072	0·0077	0·0138
X	16·42	0·053	0·00068	0·0074	0·0140
XII	20·33	0·044	0·00059	0·0069	0·0143

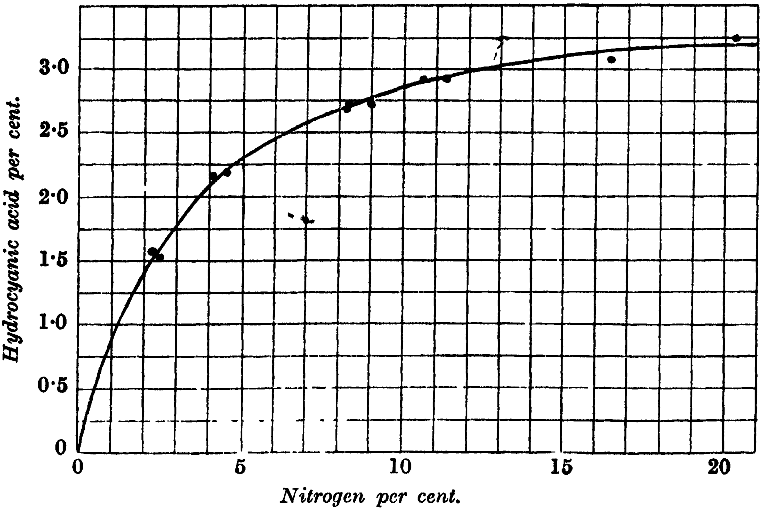
(Table I) show the degree of correspondence between the initial and the final pressures measured at 0°. In general, the final pressures are somewhat lower, except in experiment VI, where it is possible that a leak of air inwards occurred during the measurement. The difference between the values is due, as previously mentioned, to the leak of gas at the moment of explosion.

In Table II is given the percentage composition of the residual gases. The nitrogen and hydrogen figures, columns 2 and 4, are obtained by difference, and these may be compared with the experimental figures in the next columns. The agreement is within experimental error. The explosion method of estimating hydrogen was not sufficiently accurate, many results being necessary to obtain the average value given in the tables; consistent results were obtained only by burning the hydrogen with oxygen over palladium or alone over copper oxide.

In order to arrive at the gas reaction constants in Table III, the calculated percentages of hydrogen and nitrogen have been employed.

In Fig. 3 the percentage of hydrocyanic acid is plotted against residual nitrogen. A smooth curve is obtained, which suggests a logarithmic relationship, possibly due to adsorption phenomena. The ammonia is almost constant throughout. The acetylene in the residual gases varies irregularly between 1·15 and 2·76 per cent.

FIG. 3.



(except in experiment XIV : 5·53 per cent.). As a small percentage of acetylene, in the neighbourhood of the walls and ignition plugs, must escape combustion, this irregularity is to be expected. In experiment XIV, however, explosion was less complete than usual. Similar percentages of acetylene are, however, frequently found in the gases from explosive processes, so that a portion of the acetylene in the above experiments is doubtless due to a combination of hydrogen and carbon at the high temperatures in the bomb.

Conclusions.

The chemical reactions which occur during the explosion of a mixture of acetylene and nitrogen are rendered fairly clear by

Wartenberg's theoretical analysis of the possible reactions (*loc. cit.*). Acetylene may decompose according to equation (1) or (2) :

(1) $C_2H_2 = 2C + H_2 - 53000$ cals. (C amorphous).

(2) $C_2H_2 + N_2 = 2HCN - 2400$ cals.

The former is undoubtedly the principal reaction which occurs, for otherwise heat would not be liberated during the explosion. If this reaction goes to completion, and no dissociation of hydrogen occurs, it may be calculated that the temperature of explosion of pure acetylene is 3140°, whilst that of a mixture containing 10 per cent. of nitrogen is 3050°. In neither case can these temperatures be completely realised, for reaction (1) is reversible at high temperatures. This holds particularly for mixtures of nitrogen and acetylene, for not only can these substances react according to (2), but also the products of dissociation of acetylene will combine with nitrogen according to (3).

(3) $2C + H_2 + N_2 = 2HCN - 55400$ cals. (C amorphous).

Both of these reactions take place with absorption of heat, so that the theoretical maximum of temperature is never reached.

At the temperature of explosion, therefore, the principal products will be carbon, hydrocyanic acid, acetylene, hydrogen, and nitrogen. During the process of cooling to room temperature, reaction (1) and the back reactions of (2) and (3) will take place, and the percentages of the gases in the cooled mixture will depend on the rate of cooling. The rate of cooling determines the " chilling interval " during which the chemical reactions are arrested, and we should expect the mixtures containing high percentages of nitrogen, on account of their slow rate of explosion, to be chilled at a lower temperature than nearly pure acetylene. It does not seem possible to decide between equations (2) and (3) from our results, though (3) gives a better constant. Wartenberg (Table IV) showed that the equilibrium constant of equation (3) decreased with decrease in temperature.

TABLE IV.

Temp.	K.
2148° abs.	0·0097
2025	0·0041
1908	0·00157.

It is found in our experiments that the relation $[HCN]^2/[H_2][N_2]$ varies from 0·0124 with 4·13 per cent. of nitrogen to 0·0069 with 20·33 per cent. of nitrogen. The former corresponds with the equilibrium constant at approximately 1950°, and the latter with that at 1800°, whence it appears that the reactants have been chilled at a lower temperature in the mixture containing 20 per cent. of nitrogen. The effect of rate of cooling on the equilibrium constant is, however, much greater than in the case of the water-gas reaction (Andrew, T., 1914, **105**, 444), and the explanation of this perhaps lies in the nature of the heterogeneous reaction (3). The temperature coefficient of this reaction may be unusually large.

It is found that the empirical equation

$$\frac{[HCN]}{[H_2][N_2]^{0\cdot37}} = \text{a constant} = 0\cdot014$$

holds over the range 4 to 20 per cent. of nitrogen. No explanation of this relationship can be given at present.

At lower temperatures, in the neighbourhood of 1300° and 1000° respectively, reactions (4) (Bergmann, *J. Gasbeleucht.*, 1896, 117), and (5) may take place to an appreciable extent.

(4) $HCN + H_2 = C + NH_3 + 39800$ cals. (C amorphous).

(5) $N_2 + 3H_2 = 2NH_3 + 24100$ cals.

The calculations in Table III show that $[NH_3]/[H_2][HCN]$ is a constant within the experimental error of the ammonia estimation, indicating that hydrocyanic acid is the source of the ammonia.

Summary.

Mixtures of acetylene and nitrogen have been exploded at constant volume, and up to 3·24 per cent. of hydrocyanic acid has been found in the gases from the explosion. The results throw light upon the mode of production of hydrocyanic acid and ammonia in the cooling gases. The reaction constants for the equation

$$H_2 + N_2 + 2C = 2HCN$$

are found to vary between 0·0124 for 4·13 per cent., and 0·0069 for 20·33 per cent. of nitrogen in the residual gases, corresponding with a " chilling " temperature of 1950° and 1800° respectively.

The relation $\frac{[HCN]}{[H_2][N_2]^{0\cdot37}} = 0\cdot014$ has been found to hold for an explosion of mixtures of nitrogen and hydrogen at 3 atm. pressure in a closed vessel of 4 litres capacity.

The concentration of ammonia bears a close relation to the concentration of hydrocyanic acid, and it is probable that this gas is produced according to the equation

$$HCN + H_2 = NH_3 + C.$$

A new type of manometer is described for the measurement of pressures up to five atmospheres.

The authors are indebted to Professor F. G. Donnan for kindly providing the facilities for this work, and to the Department of Scientific and Industrial Research for a grant for the purchase of the phosphor-bronze bomb.

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CCXIX.—*Physical Chemistry of the Oxides of Lead. Part II. The Supposed Enantiotropy of Lead Monoxide.*

By Samuel Glasstone.

Previous authors (Ditte, *Compt. rend.*, 1882, **94**, 1310; Geuther, *Annalen*, 1883, **219**, 56; Ruer, *Zeitsch. anorg. Chem.*, 1906, **50**, 265; Germs, *Diss. Gröningen*, 1917) state that two enantiotropic forms of lead monoxide (red and yellow) must be clearly distinguished. Ruer (*loc. cit.*) suggested that the red (and reddish-brown) form of lead monoxide was stable at all temperatures below 620°, whereas the yellow form was stable only above this temperature. This suggestion was based on the fact that the red and the reddish-brown forms, if heated to 720° (at least) and 620° respectively and then allowed to cool, generate the yellow form. The reverse change could only be brought about by grinding, or by heating with concentrated (50 per cent.) alkali. The weak points in Ruer's arguments are (*a*) a cooling curve showed no break, (*b*) the red form had to be heated to a temperature 100° higher than the reddish-brown before it would give the yellow form on cooling, (*c*) a pressure of 2000 atmospheres would not change the yellow form to the reddish-brown; the grinding effect was necessary, (*d*) the reddish-brown form, either bought or obtained by grinding the yellow, was even more soluble in water than the original yellow, and (*e*) the change from the yellow to the red form had never been observed during very slow cooling from the supposed transition point downwards. Germs (*loc. cit.*), summarising previous work, emphasises the difference in colour, in density, and in solubility. As a result of his own heating experiments, he concludes that the transition point between red and yellow lead monoxide is 587°. The rate of change of the red to the yellow form is very slow at this point, but increases as the temperature rises. The brown forms (ground yellow) are said to be only partly changed to red, and therefore the change back to yellow is rapid at 587°. Attempts to change the yellow to the red form below this temperature failed unless the former was brought into solution, for example, in molten potassium nitrate at 350°; no mention is made of the possible formation of triplumbic tetroxide in this case.

By setting up half-elements of the type Pb|PbO N-NaOH, it is possible to determine the free energy of the reaction $2PbO = 2Pb + O_2$. With a transition point as high as 587°, the free energy change of this reaction at room temperature should be very different for the two forms; by repeating the determinations at other temperatures, the transition temperature might be found by extrapolation. Experimental determinations, however, led to no such appreciable differences at temperatures between 0° and 50°. Any small differences that were found, as well as the differences in physical properties (except perhaps density) mentioned by Ruer and by Germs, may be readily explained on the ground of differing states of division or agglomeration. Evidence for this view is brought forward, and explanations for the properties of the various forms of lead monoxide are developed.

EXPERIMENTAL.

The various forms of lead monoxide and N-sodium hydroxide free from carbonate were prepared as described in Part I (this vol., p. 1689).

Lead Electrodes.—Based upon previous work by Getman (*J. Amer. Chem. Soc.*, 1916, **38**, 792), Lewis and Brighton (*ibid.*, 1917, **39**, 1906), Günther (*Zeitsch. Elektrochem.*, 1917, **23**, 197), and Krahmer (*ibid.*, 1920, **26**, 97), the conclusion was drawn that in order to produce satisfactory lead electrodes the following points were to be noted: (*a*) electro-deposition with the use of a very small current density would give gradual and even deposition and thus avoid surface strains, (*b*) the use of an " addition agent " (Mathers and McKinney, *Trans. Amer. Electrochem. Soc.*, 1915, **27**, 131) would probably produce an even deposit, and (*c*) a greyish-white, microcrystalline deposit was desirable.

Ten grams of powdered Barbadoes aloes were extracted with 250 c.c. of hot water by shaking and filtering. The solid residue was roughly dried and used as the " addition agent." The bath was made up from 100 c.c. of water, 10 grams of pure lead nitrate, and 1 gram of aloes residue dissolved in 5 c.c. of glacial acetic acid. Two anodes of Kahlbaum's lead were wrapped in filter paper and suspended in the solution. The cathode, placed between the two anodes, consisted of 1 sq. cm. of platinum foil, roughened by sand paper to aid the deposit in sticking. An *E.M.F.* of 2 volts was applied and a current of 4 milliamperes (current density of 2×10^{-3} amps./cm.^{2}) passed for two hours. The cathode was then removed, well washed with recently boiled water, and immediately used in the electrode vessels. The deposit of lead was smooth and microcrystalline, of a light grey colour, and adhered well to the platinum.

Measurements.

Electrode vessels of simple type were used; they consisted of tubes 10 cm. long and 2 cm. wide, closed at the bottom and fitted with side tube and tap. The various forms of lead monoxide were filled into these vessels to a depth sufficient completely to cover the lead; the electrode solution (*N*-sodium hydroxide) was poured in and finally the lead electrode with its glass tube was inserted and gently forced in so as to leave no air in the vessel. In order to avoid the difficulty of diffusion potential, the potential of the lead half-element was measured against that of the Hg|HgO *N*-NaOH half-element, accurately defined by Donnan and Allmand (T., 1911, **99**, 845), the same solution of sodium hydroxide being used in both half-elements and also in the connecting vessel. The *E.M.F.* of this combination was measured in series with and against a standard Weston cell, a metre bridge and capillary electrometer being used for the preliminary measurements at room temperature. After measurements were taken, the lead electrode vessels were attached to the spokes of a wheel revolving twenty-four times every minute, so as to get gentle yet efficient shaking. The vessels were removed from day to day, and the potentials measured until constant and steady values were obtained.

Results.

Scale $H_2|N\text{-}H^{\cdot} = 0$. Measurements at room temperature (20°).
P.D. of Hg|HgO *N*-NaOH = 0·1140 volt at 20°.

Form of lead monoxide.*	Time after setting up (in days).					
	0	1	2	3	4	5
1. Reddish-brown	−0·558					
	−0·559				−0·559	
2. Yellowish-green	−0·561				−0·560	
	−0·559				−0·559	
3. Red	−0·552	−0·559	−0·559			−0·559
	− 0·553	−0·558				−0·560
4. R. B. by KOH	−0·555	−0·555		−0·559	−0·560	−0·560
5. Y. G. by KOH	−0·553	−0·553			−0·560	−0·560
	−0·554	−0·559		−0·559	−0·559	−0·559
6. Yellow	−0·558	−0·559		−0·560	−0·560	−0·560
7. Commercial ...	−0·552			−0·558	−0·558	−0·559
8. Ground	−0·554			−0·559	−0·560	−0·560

* For the description of these forms see this vol., p. 1690.

Results (continued).

Scale $H_2|N\text{-}H^{\bullet} = 0$. Measurements at room temperature (20°).
P.D. of $Hg|HgO$ N-NaOH = 0·1140 volt at 20°.

Form of lead monoxide.*	Time after setting up (in days). 6	7	8	9	10	Final.
1. Reddish-brown						−0·558
		−0·559	−0·559	−0·559	−0·559	−0·559
2. Yellowish-green		−0·559				−0·559
		−0·559			−0·558	−0·558
3. Red		−0·558	−0·558			−0·558
				−0·560		−0·560
4. R. B. by KOH		−0·560				−0·560
5. Y. G. by KOH						−0·560
						−0·558
6. Yellow	−0·560					−0·560
7. Commercial ...	−0·559			−0·559		−0·559
8. Ground						−0·560
	Mean ...	...	...	...	...	−0·559 volt.

* For the description of these forms see this vol., p. 1690.

Cumming (*Trans. Faraday Soc.*, 1907, **2**, 199) obtained a value of − 0·539 volt for the potential of the half-element $Pb|PbO$ (yellow) N-NaOH at 25°, without correcting for the diffusion potential between N-sodium hydroxide and N-potassium chloride solutions. The Henderson formula being used, this potential is calculated as 0·019 volt, the sodium hydroxide side being positive. The potential of the half-element alone is thus − 0·558 volt. The agreement with the result given above is satisfactory.

Discussion of Results.

Almost all the electrodes developed initial potentials up to 6 millivolts more positive than the final values, and within two or three days the different forms of lead monoxide had become adjusted to give an almost identical value in each case.

The initial high values may be due to two causes: (*a*) a metastable form of lead monoxide, being more soluble, would give higher initial values, which would diminish as this form disappeared, and (*b*) the higher initial solubility of small particles. In the first case the metastable form could be present only in very small amount, as in no instance was any alteration of the solid lead monoxide noted when the steady state was reached. The second possibility is in excellent agreement with the facts mentioned in Part I (*loc. cit.*). Almost every form of lead monoxide contains a number of very small particles having a solubility of about 0·054 gram-mol. per litre. Even the red form contains some of these particles, as can be shown by shaking a large amount of this form with a small quantity of N-sodium hydroxide solution; in this way a value of 0·055 gram-mol. of dissolved lead monoxide per litre has been obtained. The normally saturated solution of lead monoxide in *N*-sodium hydroxide contains 0·035 gram-mol. per litre. Substituting these two values in the ordinary formula for a concentration cell with bivalent ions, we find that the difference between the initial and the normal solubility corresponds with a potential of 5·5 millivolts, in agreement with the value actually found (6 millivolts).

The fact that all the forms of lead monoxide examined gave almost identical values for the final potential, shows that the free energy of the reaction, $2PbO = 2Pb + O_2$, is almost independent of the form of lead monoxide used. With the transition point of 587° suggested by Germs (*loc. cit.*), we should expect considerable differences in the free energy at the low temperature of 20°. The fact that negligible values were obtained, which could be explained on the grounds of experimental error and slight differences in solubility, is evidence in favour of a purely physical explanation for the differences between the various forms of lead monoxide.

The question of differences of free energy was further investigated at 0° and 50°, by setting up cells of the type Pb|PbO (A) *N*-NaOH PbO (B)|Pb, where A and B represent the various forms of lead monoxide in turn, and measuring their *E.M.F.*'s in series with and against a Weston cell. Slight fluctuations from the normal value of the standard cell were noted, which could be explained only on the grounds of error of experiment.

Solubility and Potential Values.

Although the potentials of the half-elements Pb|PbO *N*-NaOH had become adjusted to almost identical values, yet the main bulk of the electrode solutions varied in concentration from 0·049 to 0·029 gram-mol. of lead monoxide per litre (see this vol., p. 1692). This appears to be contradictory at first sight; the concentration that fixes the potential of the half-element, however, is that of the infinitely thin layer of solution actually in contact with the lead of the electrode. The latter is completely surrounded by a depolariser (lead monoxide) and equilibrium therefore sets in very rapidly at this point, thus giving normal potential values, although the main solution may be unsaturated or supersaturated. It has previously been shown that the solubility of the various forms of lead monoxide tends towards the same value, and we should therefore expect the same tendency in the potential of the alkaline lead–lead monoxide half-element. The difference in the solubility of the red and the yellow forms, namely, 0·035 and 0·039 gram-mol. per litre, would lead to a potential difference of 1·5 millivolts.

Definitive Measurements.

In order accurately to define the Pb|PbO *N*-NaOH half-element, to detect such differences as given above, and to find the temperature coefficient of the half-element, *P.D.* determinations were made with a Kelvin and Varley vernier potentiometer (Paul) reading to 0·0001 volt. Constant temperatures were obtained by means of a thermostat at 25·0° and a large vessel of melting ice at 0°.

The following results were obtained five weeks after setting up the electrodes, by which time the values had become quite constant.

Pb|PbO *N*-NaOH.

Yellow Form (Product No. 2).

	25°		0°
	− 0·5597 volt.		− 0·5512 volt.
	− 0·5598 „		− 0·5514 „
	− 0·5599 „		− 0·5514 „
	− 0·5597 „		− 0·5512 „
Mean	− 0·5598 „	Mean	− 0·5513 „

The temperature coefficient is − 0·00034 volt/degree.

Red Form (Product No. 3).

	− 0·5619 volt.		− 0·5537 volt.	
	− 0·5620 „		− 0·5536 „	
	− 0·5623 „		− 0·5542* „	
	− 0·5621 „		− 0·5538 „	
Mean	− 0·5621 „	Mean	− 0·5537 „	(value * omitted)

The temperature coefficient is − 0·000336 volt/degree.

In order to obtain reproducible results two conditions are necessary: (1) the lead electrode must be completely covered by the depolariser, and (2) the latter should not be disturbed in any way, so that true equilibrium may be established. Vessels of the type used for the Hg|HgO half-element are recommended.

The Effect of Carbonate.

(*a*) *In the Alkali.*—So far as was investigated, sodium carbonate in quantities up to 3·0 grams per litre had no effect on the *P.D.* of the Pb|PbO electrode (see also p. 1924).

(*b*) *In the Lead Monoxide.*—The effect in this case was to give much higher initial values, for example, − 0·550 volt, which only very gradually diminished in the course of a month. In order to get reproducible half-elements, the lead monoxide used must be free from carbonate.

Density Determinations.

Germs (*loc. cit.*) emphasises the fact that the yellow forms of lead monoxide always have a higher density than the red. From the many values given by Dammer ("Anorganische Chemie," II, (2), pp. 520 *et seq.*) it appears that the density of any form depends on its method of preparation (compare Ditte, *loc. cit.*), and that some forms of the yellow oxide have densities even lower than that of the red. A series of experimental determinations, care being taken to avoid occluded air, confirmed this conclusion.

Density at 20° compared with the density of water at 4°.

	Colour.	Preparation.	Density.
(i)	Red.	Product No. 3.	9·28
(ii)	Reddish-brown.	Product No. 1.	9·23
(iii)	Yellow.	5% boiling NaOH on $Pb(OH)_2$	9·26
(iv)	,,	10% ,, ,, ,, ,,	9·39
(v)	Yellowish-green.	20% ,, ,, ,, ,,	9·52
(vi)	Yellow.	NH_4OH on boiling basic acetate.	9·41
(vii)	,,	Commercial oxide, heated.	9·20
(viii)	,,	Product No. 1, heated.	9·53
(ix)	Reddish-brown.	No. viii, ground.	9·33
(x)	Yellow.	No. ix, reheated.	9·51

On the whole, no definite conclusions can be drawn from density measurements; we may compare the case of magnesium oxide, where the density is found to depend on the previous history of the specimen (Parravano and Mazzetti, *Atti R. Accad. Lincei*, 1921, [v], **30**, i, 63).

*Heating Experiments.**

The results are summarised below.

(1) The temperature to which any red form required to be heated in order to give the yellow form on cooling depended on the state of division. The large red particles changed rapidly at 650° (very slowly at 600—630°); the reddish-brown form (wet method) changed at 600°; the brown powders made by grinding the red form changed from 540° upwards, the temperature depending on the state of division. The supposed transition point of Germs (*loc. cit.*) is 587°.

(2) The brown forms made by very finely grinding various specimens of the yellow, required to be heated only to 540° in order to give the yellow form on cooling. This temperature, so very different from that of Ruer (620°) and that of Germs (587°), may, like the density (see above), depend on the particular form of yellow oxide used in the first place.

(3) Keeping the red form at 540° for four hours produced no visible change in colour. These results render invalid some of the conclusions of Germs (*loc. cit.*).

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* All temperatures were checked by means of a platinum resistance thermometer.

There appear to be two possible transition temperatures: (*a*) 500—600°, the minimum temperature necessary to give the yellow form on cooling, and (*b*) 350°, where the yellow colour first appears. A cooling curve should show a break in the vicinity of a transition point. A porous pot was half filled with about 300 grams of pure commercial lead monoxide and fixed vertically in an electric furnace. A thermo-electric junction was thrust well into the oxide and the whole heated to 700°. The current was then switched off and readings of temperature and time taken while the furnace cooled to 160° in three hours. No break could be detected in the region of 600° or at 350°, the curve being quite smooth along the whole of its length.

It was noted that the yellow oxide in the pot at the end of the experiment was in the form of a block, in spite of the fact that no obvious fusion had taken place and the original substance had been put in as a powder. The importance of this observation will appear later.

Since triplumbic tetroxide, on heating, always gives the yellow form of lead monoxide, it appeared possible that the production of the latter from the red form of lead monoxide was due to the intermediate formation of triplumbic tetroxide, thus:

$$\underset{\textit{Red.}}{6\mathrm{PbO}} + \mathrm{O}_2 \xrightarrow{200-450^\circ} 2\mathrm{Pb}_3\mathrm{O}_4 \xrightarrow{600^\circ} \underset{\textit{Yellow.}}{6\mathrm{PbO}} + \mathrm{O}_2$$

This suggestion was tested in two ways: (*a*) the electric furnace was heated to 600°, and a sample of the reddish-brown oxide put in; the rapid heating to 600°, at which temperature triplumbic tetroxide is completely dissociated in air, should prevent appreciable oxidation. On cooling, however, the product was yellow.

(*b*) The red and the reddish-brown oxides were heated in a current of pure nitrogen; on cooling, the colour of both specimens was yellow. These experiments proved that the colour change was not due to the intermediate formation of triplumbic tetroxide.

Crystalline Form.

There appears to be some confusion on this point. Nordenskiold (*Pogg. Ann.*, 1861, **114**, 619) found the axial ratios of crystals of yellow lead monoxide to be 1 : 0·6706 : 0·9764; he therefore concluded that the crystals were rhombic. If the ratios had been 1 : 0·6706 : 1 (within the limits of error), the crystals would have been tetragonal. Lüdecke, in Geuther's paper (*loc. cit.*), states that the crystal diagram of the red form of lead monoxide resembles that given for the yellow form by Nordenskiold, but by examination of the former in polarised light concludes that the crystal is tetragonal. The possibility of both red and yellow forms having the same crystalline structure is obvious. Within recent years, two observers have examined natural lead monoxide; Scott (*Min. Mag.*, 1914, **17**, 143) states that this substance is red with a yellowish-brown streak and that its optical characteristics suggest orthorhombic symmetry, and Larsen (*Amer. Min.*, 1917, **2**, 18) states that the central portion of the plates of natural lead monoxide consists of the yellow, orthorhombic modification, and the borders of the red, tetragonal modification. At the request of the author, Mr. J. E. Barnard kindly examined specimens of the red, reddish-brown, yellow, and yellowish-green forms of lead monoxide. He reports that the latter two forms are certainly agglomerates, and that in every case the ultimate constituent crystals appear to be identical (tetragonal) or closely allied.

The Agglomerate Theory.

All the evidence so far given is in favour of the view that the differences between the various forms of lead monoxide are attributable merely to the state of physical division. The red form, on grinding, gives brownish-yellow particles, the change of colour being due to increased reflection of white light, and it is here suggested that these brownish-yellow particles, when agglomerated, are yellow or greenish-yellow, because the agglomerates, on gentle pressure with a spatula or rubbing between paper with the fingers, give brown particles. A striking experiment in favour of this view is the following. Lead hydroxide of the formula $3PbO,H_2O$ can be prepared in comparatively large crystals (1 mm. in diameter). When these crystals are heated, yellow lead monoxide is obtained, the shape of the original crystals being retained, but when the crystals are first ground and then heated, the resulting lead monoxide is reddish-brown.

Explanation of the Variation of Colour.

It is suggested that all forms of lead monoxide reflect green light and transmit red, the violet end of the spectrum being absorbed. In the case of the yellow and the green agglomerates, owing to the enormous number of internal surfaces, the red light is lost by internal reflection (and eventual absorption), and therefore only the green colour is visible. With a smaller loss of red light the yellowness would increase, whilst the larger agglomerates would be more green in colour. In the microscopic examination, the transmitted red light could occasionally be seen. A very similar case to the one under discussion occurs during the precipitation of gold sols. These sols contain green particles which, on agglomerating, appear brown; the particles here probably transmit green light and reflect red, and therefore give in the reverse order the effects displayed by lead monoxide.

Changes on Heating.

The theory is proposed that when the comparatively large crystals of red lead monoxide are heated, splintering into smaller particles takes place at some temperature (600—650°), possibly due to unequal expansion in different directions. These smaller particles still adhere together on cooling and in this way form the yellow agglomerates of brown particles. When the agglomerates are crushed, the constituent brown particles become visible.

In the case of the reddish-brown or brown forms, at a certain temperature (540—600°) the very fine particles fuse; thus a large number of small particles join together and agglomerate on cooling by the process of sintering. Confirmation of this view is found in the fact noted on p. 1921, that powdered lead monoxide, heated to 700°, is recovered on cooling in the form of a yellow block. Reinders and Hamburger (*Zeitsch. anorg. Chem.*, 1914, **89**, 71) state that the available surface of yellow lead monoxide decreases on heating owing to the particles sintering together. The temperature at which sintering takes place depends of course on the size of the particles, and in this fact is found the explanation of the variation in the temperature to which the different forms have to be heated in order that they shall give the yellow form on cooling (p. 1920). (The melting point of lead monoxide is given in Watt's Dictionary of Chemistry, 1892, as 585—630°; the latest value, given by Germs [*loc. cit.*] and others, is 875°.)

These assumptions account for the different temperatures at which the conversion of the red form, and of the series of brown and yellowish-brown powders made by grinding this form, into the yellow variety occurs. The irreversibility of the change from the yellow to the red form by slow cooling (compare Germs, *loc. cit.*; Ruer, *loc. cit.*) is obvious; dissolution is an essential, intermediate step.

These suggestions offer explanations of the properties of the various forms of lead monoxide on purely physical grounds, without involving enantiotropic changes.

The Solubility Product of Lead Monoxide at 25°.

Using the value $-$ 0·562 volt as the potential of the Pb|PbO (red) *N*-NaOH electrode, and $-$ 0·130 volt as the normal electrode potential of lead at 25° (Lewis and Brighton, *loc. cit.*; Getman, *J. Amer. Chem. Soc.*, 1918, **40**, 611), we obtained $2{\cdot}27 \times 10^{-15}$ gram-ion per litre as the concentration of lead ions in *N*-sodium hydroxide saturated with red lead monoxide. The hydroxyl-ion concentration in this solution is 0·72 gram-ion per litre. The solubility product of lead monoxide is thus given by

$$L = [\mathrm{Pb}^{\cdot\cdot}][\mathrm{OH}']^2 = 2{\cdot}27 \times 10^{-15} \times 0{\cdot}72 \times 0{\cdot}72 = 1{\cdot}17 \times 10^{-15}.$$

The concentration of lead ions in a solution of lead monoxide in water is approximately $\sqrt[3]{\ }_{4}$, that is, about $0{\cdot}66 \times 10^{-5}$ gram-ion per litre. The solubility of red lead monoxide in water is $0{\cdot}26 \times 10^{-3}$ gram-mol. per litre. This rough comparison emphasises the uncertainty of the ionisation of lead monoxide in water, and the futility of determining the solubility of lead monoxide or hydroxide in water by the conductivity method (compare Pleissner, *Arb. Kaiser. Gesundh.-Amt.*, 1907, **26**, 384).

The Effect of Carbonate.

In order to alter the potential of the alkaline lead electrode, the addition of carbonate must affect the concentration of the lead ions, by being present in an amount sufficient to make the product of $[\mathrm{Pb}^{\cdot\cdot}]$ and $[\mathrm{CO}_3'']$ exceed the solubility product of lead carbonate, which is $3{\cdot}3 \times 10^{-14}$ (Pleissner, *loc. cit.*). To reach the solubility product of lead carbonate, the CO_3'' concentration must be $\frac{3{\cdot}3 \times 10^{-14}}{2{\cdot}3 \times 10^{-15}}$, that is, 14 gram-ions per litre, which is, of course, impossible under the conditions of working. Assuming, as we have done, that the carbonate does not affect the concentration of hydroxyl ions, it will have no appreciable effect on the potential of the Pb|PbO *N*-NaOH electrode.

Dissociation Pressures.

The cell Pb|PbO *N*-NaOH H_2 (1 atm.)|Pt, whose *E.M.F.* is $-0{\cdot}562 - (-0{\cdot}809) = 0{\cdot}247$ volt, may be regarded as an $H_2 - O_2$ cell, with oxygen supplied at the dissociation pressure of the reaction $2\mathrm{PbO} \longrightarrow 2\mathrm{Pb} + \mathrm{O}_2$, at 25°. Using the value 1·226 volts as the *E.M.F.* of the $H_2 - O_2$ cell with both gases at atmospheric pressure at 25°, and substituting the values in the formula connecting the *E.M.F.* of these gas cells with the pressure of the gases, we find that the dissociation pressure of oxygen produced by the decomposition of red lead monoxide at 25° is $4{\cdot}2 \times 10^{-67}$ atm.

By the use of Nernst's theorem, the dissociation pressure can be calculated when it is known that the heat absorbed in the dissociation is 100,600 calories per gram-mol. of oxygen (Thomsen); the result obtained is $1{\cdot}9 \times 10^{-67}$ atm. at 25°. Considering the low order of magnitude of these values, the agreement is satisfactory.

The temperature at which the dissociation pressure in the above reaction is equal to 0·21 atm. is the temperature at which lead monoxide will decompose completely if heated in air. This temperature can be calculated by three methods, it being assumed that both lead monoxide and lead remain solid.

Method 1.—If the cells Pb|PbO alkali H_2|Pt and H_2 (1 atm.) — O_2(0·21 atm.) are imagined to have their temperature raised until both have the same *E.M.F.*, we know that at this temperature lead monoxide will have a dissociation pressure of 0·21 atm. The *E.M.F.* of both these cells is known at 25°, and their temperature coefficients may be calculated by applying the Gibbs-Helmholtz equation to the known heats of reaction. Assuming that these coefficients remain constant over a considerable range of temperature, we find that the *E.M.F.*'s would become equal at 2600° abs. At this temperature lead monoxide would completely decompose if heated in air.

Method 2.—Using the integrated form of the van't Hoff isochore, where partial pressures are involved, we get $R \log_e K_p = -\frac{Q_p}{T} + C$, where Q_p is the heat absorbed, and C is an integration constant. The latter can be evaluated as follows. If the ratio of the concentrations of lead monoxide and lead can be considered constant at all temperatures, we can replace K_p in the above expression by p_{O_2} at any temperature. For 298° abs. we have found that p_{O_2} is equal to $4{\cdot}2 \times 10^{-67}$, and taking Q_p as 100,600 cals., we obtain $C = 32{\cdot}0$. Assuming that Q_p remains constant, it is found that p_{O_2} is equal to 0·21 atm. at 2860° abs.

Method 3.—Stahl (*Metallurgie*, 1907, **4**, 682), using Nernst's formula, has calculated that the temperature at which the pressure of oxygen in the system under discussion becomes equal to 0·21 atm. is 2348° abs.

Considering the approximations involved in connexion with the pressures of lead monoxide and lead, and with the various heats of reaction, the agreement between the three methods is good.

Heat of the Reaction $Pb + \frac{1}{2}O_2$ (1 atm.) $= PbO$ *at* 25°.

This value can be calculated from electrochemical data by the use of the Gibbs-Helmholtz equation. The *E.M.F.* of the cell Pb|PbO (red) *N*-NaOH H_2|Pt is 0·2469 volt at 25°, and 0·2603 volt at 0° (from the known potentials of the two electrodes). The temperature coefficient is thus – 0·00054 volt/degree. The total energy of the reaction

$$PbO + H_2 \text{ (1 atm.)} = Pb + H_2O \text{ (liquid)}$$

at room temperature is then calculated as 18,790 cals. Taking the heat of formation of liquid water as 68,400 cals., we obtain 49,610 cals. as the heat of formation of red lead monoxide at room temperature. The thermochemical value (Thomsen) 50,300 cals., the form of lead monoxide not being stated, is probably less accurate than the electrochemical value.

Calculation of E.M.F. *by Nernst's Theorem.*

Using the method of Nernst (*Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 247), it is possible to calculate the *E.M.F.* of the cell $Pb|PbO - H_2|Pt$ at 0°. The reaction involved is

$$PbO + H_2 = Pb + H_2O,$$

the water being in the form of ice. For this reaction at 17°, we have:

$$Q_T = 68{,}400 \text{ (H,O)} + 1580 \text{ (ice, water at 17°)} - 50{,}300 \text{ (Pb,O)} = 19{,}680 \text{ cals.}$$

The molecular heats of reactants and resultants are taken as 11·8 for lead monoxide, 6·8 for hydrogen, 6·4 for lead, and 9·5 for ice. The difference between the molecular heats of the reactants and of the resultants is 2·7 cals., leading to a value of – 0·0014 for β (Nernst, *loc. cit.*), and thus $Q_0 = 18{,}783$ cals. Assuming that the "chemical constant" for hydrogen is 1·6, we obtain the figure 0·251 volt as the *E.M.F.* of the above cell at 0°. The experimental value is 0·260 volt at 0°, with water instead of ice as one of the products of the reaction. The heat of formation of lead monoxide being taken as 49,610 cals. (see above), the *E.M.F.* is calculated as 0·265 volt.

Using a more approximate method in which water is involved instead of ice, we get $Q_T = 18{,}100$, $\beta = - 0{\cdot}016$, and Q_0 is thus 18,430. The value for the *E.M.F.* of the cell at 25° is then 0·257 volt, the actual experimental value being 0·247 volt.

Summary.

(1) The results of measurements of the $Pb|PbO$ *N*-NaOH potential are not in harmony with the theory that lead monoxide is enantiotropic.

(2) The temperature to which the red form of lead monoxide has to be heated in order to give the yellow form on cooling, depends on the state of division of the former.

(3) Crystallographic evidence is shown to be very confusing.

(4) The difference in properties of the various forms of lead monoxide is explained on the grounds of degree of sub-division or agglomeration.

(5) The solubility product of red lead monoxide is $1{\cdot}17 \times 10^{-15}$ at 25°.

(6) The dissociation pressures of oxygen derived from lead monoxide are calculated by various methods which give good agreement.

(7) The heat of formation of red lead monoxide is 49,610 calories.

(8) The *E.M.F.*'s calculated by Nernst's theorem are in good agreement with the experimental values.

The author desires to thank Professor Allmand for suggesting the work and for criticism and advice, and also Mr. J. E. Barnard for kindly undertaking the crystallographic examination of the various forms of lead oxide.

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CCXX.—*Investigations into the Analytical Chemistry of Tantalum, Columbium, and their Mineral Associates. I. The Use of Tartaric Acid in the Analysis of Natural Tantalocolumbates. II. The Separation of Zirconium from Tantalum and from Columbium.*

By WALTER RAYMOND SCHOELLER and ALAN RICHARD POWELL.

ONE of the most difficult problems that confront the mineralogist is the analysis of the tantalo- and titano-columbates. Not only are these minerals of the greatest complexity as regards both the number and the nature of the elements of which they are made up, but also the separate estimation of tantalum, columbium, and titanium in presence of each other is up to now more or less approximate, and their separation from many other elements is beset with uncertainties. It is due chiefly to the difficulties encountered in their analysis that the true chemical affinities of the minerals in question are not yet quite clearly understood.

The present research, which it is intended shall be as comprehensive as possible, aims at improving the state of our knowledge of these minerals by testing the accuracy of published analytical methods and, if possible, by improving them and devising new ones. For some time past the authors have been studying the literature on the subject and investigating methods in the laboratory. The conclusions drawn by other workers in this field are frequently contradictory, and a repetition of some of the earlier work is needed in order to clear up debatable points. As the authors' time available for this investigation is limited, they have enrolled the help of collaborators, who will report on the result of their labours in due course. The whole research will form a connected series of papers appearing under the above general title.

I. *The Use of Tartaric Acid in the Analysis of Natural Tantalocolumbates*

This section is in the nature of a preliminary communication, being devoted to certain considerations on the analysis of tantalocolumbates and the brief description of a method of analysis which we have worked out and intend to elaborate more fully; so far it has given promising results with tantalite and columbite.

The best known and most generally applied method for the analysis of minerals of this group is what will hereafter be termed the pyrosulphate-hydrolysis method, that is, decomposition of the mineral by fusion with alkali pyrosulphate followed by prolonged boiling of the solution of the melt in order to precipitate the earth acids. This procedure is by no means above criticism, but as far as the decomposition of the mineral is concerned we feel strongly inclined to favour pyrosulphate as having a wider range of usefulness than potassium hydroxide or carbonate, potassium hydrogen fluoride, or hydrofluoric acid. As regards the hydrolysis of the solution resulting from the pyrosulphate melt, this process has several disadvantages; thus, the earth acids are not precipitated completely if the acidity of the solution is too great; the complete precipitation of the earth acids is not easily ascertained; and the precipitate—whether the acids are completely precipitated or not—is always contaminated with other elements, some of which are wholly, others partly, precipitated (silica, titania, tungsten, tin, antimony, iron, zirconia). It is opportune here to recall that two elements in presence of each other may lose their individuality; or "the reactions these elements undergo when they occur alone do not necessarily occur when the two elements are mixed together" (Mellor, "Quantitative Inorganic Analysis," 1913, p. 496). For example, columbium by itself is most difficult to precipitate completely by hydrolysis, but the presence of even a small quantity of tantalum causes complete precipitation (Meyer and Hauser, "Die Analyse der seltenen Erden und der Erdsäuren," p. 183). Titanium has the reverse effect on columbium, as it impedes the precipitation (Mellor, *op. cit.*, p. 420), whilst the hydrolysis of titanium is adversely affected by zirconium (Hillebrand, *Bull. Geol. Survey U.S.A.*, No. **422**, p. 136). Therefore, if only the four elements named are present in the solution, the process of hydrolysis is a sufficiently complex reaction, which is at present being investigated.

The impure precipitate produced by hydrolysis must next be resolved into its constituents, and this again is a troublesome procedure. The first step consists in dissolving the earth acids in a suitable solvent, filtering off any residue, and again hydrolysing the filtrate. Three solvents are mentioned in the literature: (1) Basic ammonium tartrate, by Hoffmann and Prandtl (*Ber.*, 1901, **34**, 1064): they merely state that the precipitate obtained after the hydrolysis was extracted with the compound mentioned. (2) Mannitol (Hauser, *Zeitsch. anorg. Chem.*, 1908, **60**, 231; Hauser and Herzfeld, *Centr. Min.*, 1910, 758): the precipitate is treated with a 20 per cent. potassium hydroxide solution containing 10 per cent. of mannitol, the insoluble gangue filtered off, and the filtrate freed from lead and iron by ammonium sulphide. The filtrate is boiled under reflux, any zirconium remaining in solution; the reprecipitated earth acids are still accompanied by titanium, tin, antimony, and silica. (3) Hydrogen peroxide (Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, **64**, 65): the precipitate obtained by the hydrolysis is digested with 10 per cent. sulphuric acid and an equal volume of 3 per cent. hydrogen peroxide; the residue consists of gangue, silica, and lead sulphate. The filtrate is again submitted to hydrolysis with sulphurous acid, which precipitates tantalum, columbium, titanium, tungsten, tin, and antimony; iron and zirconium remain dissolved.

Regarding the last-named process, it must here be mentioned that divergent views have been expressed on the solubility of tantalic acid in hydrogen peroxide. Noyes (*Chem. News*, 1906, **93**, 180) found that it remained in large part undissolved, but Giles (*ibid.*, 1907, **95**, 1) showed that it dissolved completely "when diffused in dilute hydrochloric or sulphuric acid on addition of *sufficient* pure hydrogen peroxide (Merck's 'perhydrol')." In a recent communication, however, Hahn and Gille (*Zeitsch. anorg. Chem.*, 1920, **112**, 283) report that tantalic acid precipitated from hot solutions is almost insoluble, and when precipitated in the cold is very slightly soluble, in acid hydrogen peroxide; and that it reduces the solubility of columbic and titanic acids. They draw the conclusion that Weiss and Landecker's method is inapplicable in presence of tantalic acid. In view of these conflicting statements, it would seem that the matter must be once more investigated.

The second step in the purification of the precipitate obtained by the hydrolysis consists in removing tungsten, tin, and antimony by digestion with ammonium sulphide (Berzelius) or by fusion with sodium carbonate and sulphur (Rose). These methods have however been condemned by Giles (*Chem. News*, 1909, **99**, 1), Smith (*Proc. Amer. Phil. Soc.*, 1905, **44**, 40), and Blomstrand (*J. pr. Chem.*, 1919, [ii], **99**, 40). Giles separates tin and antimony from the earth acids by fusion with potassium carbonate, solution of the melt in citric acid, and precipitation of tin and antimony by hydrogen sulphide; we propose the somewhat similar process described below. The methods for the separation of tungsten will shortly be submitted to a critical study.

Authors' Proposed Method.—The above considerations induced us to seek improvements in the analysis of tantalum–columbium minerals by evolving a different process while retaining pyrosulphate as a flux. The guiding idea was to avoid an initial hydrolysis for the precipitation of the earth acids and to attempt a preliminary purification of the solution by the removal of as many metals as possible, followed by a modified or improved process of hydrolysis. Now it is well known that tartaric acid prevents the precipitation of the hydroxides of tantalum, columbium, titanium, etc., and we ascertained that a concentrated solution of tartaric acid dissolves the cake from the pyrosulphate fusion of the minerals in question to a perfectly clear solution (compare Powell, *J. Soc. Chem. Ind.*, 1918, **37**, 285T). We fuse 1 gram of the finely powdered mineral with 6 grams of sodium pyrosulphate in a silica crucible, adding sulphuric acid and again fusing if the melt solidifies before the decomposition is complete, and leach the cold mass with a solution of 10 grams of tartaric acid in not more than 50 c.c. of water. The insoluble residue contains any quartz, cassiterite, gangue, lead sulphate, and possibly some unattacked mineral; if this should be the case, fusion with pyrosulphate and extraction with tartaric acid are repeated on the ignited residue, when all the decomposable material is obtained in solution. The residue is analysed for lead, tin, silica, etc., whilst the combined filtrates are saturated with hydrogen sulphide; in this manner antimony, copper, traces of tin, and any other metals of the hydrogen sulphide group are eliminated and estimated. The filtrate, on digestion with ammonia and ammonium sulphide, yields a precipitate containing all the iron and uranium, as well as a small part of the manganese, if this metal be present. Manganese, as is known, is but imperfectly precipitated as sulphide from tartrate solutions (compare Mellor, *op. cit.*, p. 363).

The operations so far described eliminate certain rather troublesome elements (for example, silica, iron, tin, antimony), whilst tantalum and columbium are in solution, still accompanied by a number of their mineral associates. The following may be present: tungsten, titanium, and zirconium; rare-earth metals and thorium; aluminium, glucinum, manganese, calcium, and magnesium. We are now striving to find an accurate and comparatively simple method to resolve this complex mixture into its components.

We have already investigated, but without success, a scheme for separating titanium and zirconium as phosphates from tantalum and columbium in tartaric acid solution. We ascertained that ammonium phosphate does not precipitate the earth acids from tartrate solutions containing free tartaric acid, even on boiling, whilst zirconia is not precipitated in the cold, but boiling causes quantitative precipitation. It seemed therefore possible to separate zirconium from tantalum and columbium by leaching a pyrosulphate melt of the mixed oxides with sodium hydrogen tartrate and adding ammonium phosphate to the boiling solution. Under these conditions, however, when zirconia by itself would have been precipitated as phosphate, no precipitate was obtained in presence of tantalum and columbium, which provides another example of "loss of individuality." It was only when a fair excess of sulphuric acid was added to the solution that precipitation ensued, but the results calculated to zirconia were too high, due to contamination with several units per cent. of earth acids. As regards titania, this was only slowly and incompletely precipitated by ammonium phosphate from tartrate solutions acidified with sulphuric acid.

Summary.

The usual procedure for the analysis of tantalum–columbium minerals is briefly discussed. A new method of analysis is outlined, in which the initial hydrolysis is avoided by solution of the pyrosulphate melt in tartaric acid solution.

II. *The Separation of Zirconium from Tantalum and from Columbium.*

The pyrosulphate–hydrolysis method, outlined in section I of this paper, is so far the only one available for separating zirconium from tantalum and columbium, Bailey's hydrogen peroxide method

(T., 1886, **49**, 149, 481) having proved untrustworthy (Meyer and Hauser, *op. cit.*).

A process of separation, based on an entirely different principle, was indicated by Hauser and Herzfeld in a paper on an occurrence of blomstrandine in the Urals (*Centr. Min.*, 1910, 758). They give a very brief outline of the procedure used in analysing the mineral, and state that they intended shortly afterwards to publish a detailed description of the most up-to-date procedure for the analysis of minerals of the earth acids—an intention which does not appear to have been carried out. The published method includes the following particulars for the separation of zirconia from the earth acids. The mixed oxides are fused with potassium hydroxide in a silver dish, the melt being continually stirred with a silver spatula; the melt is extracted with water and the residue filtered off; this is ignited and again fused as before. The insoluble residue from the second fusion is to be regarded as zirconia ("*ist als Zirkonerde anzusehen*") which must, however, still be tested for the presence of titania. The proportions of the constituents in question are reported thus: $Cb_2O_5 = 15{\cdot}08$; $Ta_2O_5 = 1{\cdot}30$; $ZrO_2 = 0{\cdot}50$ per cent.

The wording of the above quotation referring to the purity of the residual zirconia is rather guarded, and as far as we know, no critical study of the potassium hydroxide fusion has yet been published. Giles pointed out (*Chem. News*, 1909, **99**, 1) that zirconia was unaffected by fusion with potassium carbonate, and expressed the opinion that this might answer as a means of separating zirconia from tantalum and columbium. He did not carry out any test separations to prove that the method was quantitative. We therefore decided to investigate it by working with the pure oxides. Those of tantalum and columbium were prepared from the carefully recrystallised double fluorides, whilst the zirconia was obtained from recrystallised zirconyl chloride prepared from zircon.

For reasons explained below we confined ourselves almost entirely to the use of potassium carbonate. In a preliminary experiment, 0·25 gram of each oxide was fused by itself with 2·5 grams of potassium carbonate in a platinum crucible; the melt was leached with hot water, the solution filtered off, acidified with hydrochloric acid, and boiled with a slight excess of ammonia and filter-pulp; the precipitate was ignited and weighed. The filter containing the residue from the fusion was washed with dilute hydrochloric acid to remove any potassium salt, the liquid boiled, made ammoniacal, and again filtered through the same paper, which was ignited and the residue weighed; in the case of tantalum and columbium pentoxides this residue was again fused with 2 grams of potassium carbonate, giving a second soluble fraction and a final residue. It is interesting to note the ease with which columbium pentoxide is attacked by potassium carbonate at the melting point of the salt, whilst the reaction between tantalum pentoxide and potassium carbonate requires the heat of a very powerful blast burner. The weight of the final products was in excess of that originally taken owing to unavoidable contamination: we were unable to obtain chemically pure potassium carbonate, and the best article procurable was not quite free from silica and iron. In addition, the crucible was more or less strongly corroded by the fused alkali, which led to further contamination by platinum. The results of the preliminary tests are tabulated below.

Weight of substance taken. Gram.		Weight of products.			
		From first fusion.	From second fusion.	Total products.	Remarks.
0·2512 ZrO_2	Insoluble	0·2562	—	0·2562	
	Soluble	0·0013	—	0·0013	black (Pt).
0·2503 Ta_2O_5	Insoluble	0·0242	0·0074	0·0074	black.
	Soluble	0·2285	0·0182	0·2467	
	Insoluble	0·0090	0·0012	0·0012	brown.
	Soluble	0·2434	0·0068	0·2502	

The following procedure was used in the test separations. The pure weighed oxides were fused with potassium pyrosulphate in a silica crucible until a clear melt was obtained; this was leached with water and the turbid liquid boiled with filter-pulp and a slight excess of ammonia. The precipitate was filtered off, washed with dilute ammonium nitrate solution, and strongly ignited in a platinum crucible. This preliminary treatment resulted in the production of an intimate mixture of finely divided oxides such as would be obtained in an analysis. The mixed oxides were fused with potassium carbonate (5 to 20 parts) over a powerful blast burner until the fusion was tranquil. The cold melt was leached with hot water in platinum or porcelain and the liquid filtered through close-textured paper. It was, as a rule, necessary to re-filter once or even twice through the same paper, as the finely-divided zirconia gave a turbid filtrate at the start. The insoluble residue was washed with 2 per cent. potassium carbonate solution. The filtrate was acidified with hydrochloric acid and boiled with filter-pulp and a slight excess of ammonia; the precipitate was filtered off, washed with water containing ammonium nitrate, strongly ignited in a platinum crucible, and weighed. The residue from the leaching of the melt was washed with dilute hydrochloric acid, the washings were boiled with a slight excess of ammonia, again filtered through the same paper, the latter was ignited with the residue and weighed; the weighed residue was again fused with potassium carbonate, etc., giving a second soluble fraction and residue. The latter was fused a third time, yielding a third soluble fraction and a final residue (zirconia). The precipitates from the three soluble fractions (tantalic acid) were combined. In the separation of zirconia from columbium pentoxide only two fusions were made.

The final products were purified in the following manner. The zirconia residue was fused with pyrosulphate and the melt leached with cold dilute sulphuric acid to prevent the precipitation of the small quantity of tantalic acid present. The solution was precipitated with hydrogen sulphide after addition of a little filter-pulp for the purpose of collecting the platinum sulphide; the precipitate was filtered off, well washed, ignited, and weighed; it was then fused with a little pyrosulphate, the melt leached with concentrated tartaric acid solution, and the residue filtered off, ignited, and again weighed to ascertain its freedom from tantalic acid; the difference between the first and second weight, if any, was added to the weight of the zirconia. The filtrate from the platinum sulphide was nearly neutralised with sodium carbonate, and boiled for an hour with sodium thiosulphate. The precipitate was filtered off, washed, ignited, leached with dilute acid, the liquid made slightly ammoniacal, filtered again through the same paper, and the washed precipitate ignited and weighed as zirconia.

The combined tantalic (columbic) acid fractions were fused with pyrosulphate in a silica crucible; the melt was leached with concentrated tartaric acid solution, the residue filtered off, ignited, and again fused as before. The melt was again leached with tartaric acid solution, and the two combined leach liquors were treated with hydrogen sulphide and a little filter-pulp. The precipitate, containing platinum and any siliceous matter present, was filtered off, washed, ignited, and weighed. This weight was subtracted from that of the combined earth acid fractions, and the difference reckoned as tantalum (columbium) pentoxide. The table on page 1935 shows the results obtained.

The figures prove that the amount of tantalic acid rendered soluble in the first fusion was independent of the proportion of potassium carbonate used: in expts. 14—17 this amounted to 2·5 grams; in expt. 18, to 5 grams; and in expt. 20, to 10 grams.

In expt. 19, the mixed oxides were fused with 3·5 grams of potassium hydroxide in a nickel crucible, at first gently for half an hour, then strongly for twenty minutes. The result shows that potassium hydroxide is less effective than the carbonate, which is to be ascribed to the lower temperature at which the fusion is necessarily conducted; at a red heat, the fused alkali creeps over the edge of the crucible, and contamination of the melt with nickel becomes pronounced. The use of potassium hydroxide was therefore abandoned.

Expt.	Weight of substance taken. Gram.		Weight of products. From first fusion.	From second fusion.	From third fusion.	Total products.	Purified oxides.	Error.	Grams of K_2CO_3 used in each fusion.
14	0·2504 ZrO_2	Insoluble	0·2930	0·2594	0·2554	0·2554	Not purified.		(1) 2·5 (2) 2 (3) 2
	0·2501 Ta_2O_5	Soluble	0·2134	0·0324	0·0066	0·2524			
15	0·2510 ZrO_2	Insoluble	0·3496	0·2644	0·2562	0·2562	0·2530	+0·0020	(1) 2·5 (2) 2 (3) 2
	0·2504 Ta_2O_5	Soluble	0·1658	0·0764	0·0090	0·2512	0·2482	−0·0022	
16	0·2503 ZrO_2	Insoluble	0·2700	0·2686	0·2614	0·2614	0·2589	+0·0086	(1) 2·5 (2) 2·5 (3) 2·5
	0·2495 Ta_2O_5	Soluble	0·2318	0·0035	0·0122	0·2475	0·2414	−0·0081	
17	0·0126 ZrO_2	Insoluble	0·0486	0·0272	0·0214	0·0214	0·0186	+0·0060	(1) 2·5 (2) 1 (3) 2·5
	0·2502 Ta_2O_5	Soluble	0·2186	0·0205	0·0120	0·2511	0·2461	−0·0041	
18	0·2534 ZrO_2	Insoluble	0·3028	0·2726	0·2682	0·2682	0·2588	+0·0054	(1) 5 (2) 3 (3) 3
	0·2509 Ta_2O_5	Soluble	0·2174	0·0342	0·0086	0·2602	0·2476	−0·0033	
19	0·2511 ZrO_2	Insoluble	0·3475	0·2970	—				(1) 3·5 (2) 3 KOH
	0·2520 Ta_2O_5	Soluble	0·1657	—	—				
20	0·2521 ZrO_2	Insoluble	0·3083	—	—				(1) 10
	0·2530 Ta_2O_5	Soluble	0·2200	—	—				
21	0·2509 ZrO_2	Insoluble	0·2661	0·2563	—	0·2563	0·2515	+0·0006	(1) 5 (2) 3
	0·2520 Cb_2O_5	Soluble	0·2673	0·0045	—	0·2718	0·2511	−0·0009	
22	0·2504 ZrO_2	Insoluble	0·2551	—	—	0·2551	0·2512	+0·0008	(1) 5
	0·2502 Cb_2O_5	Soluble	0·2514	—	—	0·2514	0·2498	−0·0004	

Conclusions.

The separation of zirconia from columbium pentoxide by fusion with potassium carbonate is quantitative within the limits of experimental error. It is advisable to submit the fusion residue to a second fusion.

The separation of zirconia from tantalum pentoxide by fusion with potassium carbonate is less satisfactory than the preceding. Even after three fusions, the results show a positive error of 2—8 mg. for zirconia, and a corresponding negative error for tantalum pentoxide. Roughly speaking, 80 to 90 per cent. of the tantalic acid present is rendered soluble in the first fusion.

The fusion method described in this section should prove more especially useful for estimating zirconia in columbate minerals poor in tantalum. It may also be applied in the analysis of tantalo-columbates for checking the purity of zirconia precipitates, or ascertaining the presence of small quantities of zirconia in precipitates obtained by the usual method of hydrolysis.

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CCXXI.—*Catalysis of the Mutarotation of Dextrose by Metals.*

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IN the course of experiments on the action of an electromagnetic field on the mutarotation of dextrose, it was observed that a field of approximately 20,000 gauss affected neither the rate of change of the reaction nor the concentration of the equilibrium mixture. A marked acceleration of the mutarotation was, however, noticed on repeating the experiments with nickel in the polarimeter tube. This phenomenon was subsequently shown to be due to the direct catalytic activity of metallic nickel, and not to any superimposed electromagnetic effect. Very little work appears to have been done on the effect of metal surfaces on the mutarotation of sugars, and no reference has been found in the literature to the catalytic effect of metals like nickel. The platinum metals have, however, been shown by Plzak and Husek (*Zeitsch. physikal. Chem.*, 1904, **47**, 733) to catalyse the rate of inversion of sucrose.

The mutarotation of dextrose is markedly accelerated by catalysts producing hydroxyl ions, and to a less extent by hydrogen ions, and it was possible that the function of the metal was to supply one of these ions. On the other hand, the catalysis of hydrogenation processes by metallic nickel made it possible that the acceleration was caused by some surface action. The observation was thus of interest, and an investigation promised to throw light on catalysis by metallic nickel in hydrogenation processes.

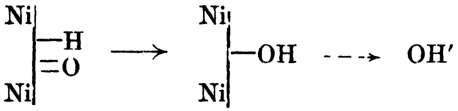
The greater part of the work described in the present communication has been carried out with metallic nickel, but preliminary experiments have shown that the nickel may be replaced by cobalt, iron, and copper. The dextrose could also be replaced by other sugars. The activity of the metals was considerably increased by a preliminary oxidation and reduction of the surface, and the temperature at which the reduction was carried out had an important bearing on the activity of the metal. The best temperature for the reduction of the nickel was 340—440° ; when reduced above or below these temperatures, the metal shows a much smaller activity.

The action of the catalyst was not uniform from the beginning to the end of the reaction; there was an induction period in the beginning, and a decline in the activity of the catalyst towards the end. This decline in the activity of the catalyst is a phenomenon which is frequently observed in hydrogenation with metallic nickel (Willstätter and Waldschmidt-Leitz, *Ber.*, 1921, **54**, [*B*], 113).

The decrease in the activity of the surface was accompanied by the dissolution of some of the metal. This dissolved or dispersed metal is still active in solution, as was demonstrated by adding it to a freshly prepared dextrose solution. The activity of the solution, however, declines slowly; a change which is probably associated with the formation of a compound of the metal with dextrose.

The surfaces of cobalt and nickel are attacked by water, with the formation of hydroxide and the liberation of hydroxyl ions. The surface of the reduced metal is attacked more rapidly than that of either the untreated or oxidised metal. The rapidity of production of hydroxyl ions by the metal runs roughly parallel with its effect as a catalyst on the mutarotation of dextrose. Thus cobalt, which gives rise more readily to hydroxyl ions than metallic nickel, is also the more effective as a catalyst.

It is difficult to state definitely the source of this hydroxyl ion. Since the catalysis is not decreased by the replacement of the oxygen in the water by hydrogen, it is evident that dissolved oxygen plays but a small part. There appear to be two alternative sources, (*a*) a sub-oxide of the metal, and (*b*) adsorbed hydrogen and oxygen on the surface. In the former case hydroxyl ions would be formed by the interaction of the oxide with water, and in the latter case the adsorbed gases could unite in the presence of water to give this ion. Thus:



$$\begin{array}{l|l} \text{Ni} & \\ & -\text{H} \\ & =\text{O} \\ \text{Ni} & \end{array} \longrightarrow \begin{array}{l|l} \text{Ni} & \\ & -\text{OH} \\ \text{Ni} & \end{array} \dashrightarrow \text{OH}'$$

The catalytic activity of the metals in the platinum group is generally ascribed to the presence of hydrogen and oxygen. Mond, Ramsay, and Shields (*Phil. Trans.*, 1898, [*A*], **191**, 105) showed that both hydrogen and oxygen can exist together in metallic palladium. Willstätter (*loc. cit.*) emphasises this point and puts forward a theory of catalysis in which the catalyst is a compound of platinum with both hydrogen and oxygen. Brochet expressed an opinion that pure nickel is catalytically inactive, and this has recently been confirmed by Willstätter, who finds that the most readily reduced organic compounds cannot be hydrogenated in the presence of nickel which has been completely freed from oxygen. This inactive nickel can, however, be activated by priming with oxygen.

It thus appears that the source of the hydroxyl ions is either the sub-oxide or the hydrogen and oxygen adsorbed on the nickel or cobalt surface. This is in accordance with the experiments with oxidised metals; the activity of an oxidised metallic surface is always much smaller than that of a reduced surface. An explanation is also provided for the relative inactivity of metallic nickel, when reduced at high temperatures, for in this case the dissolved or combined oxygen is probably almost completely removed.

The catalysis by nickel is almost entirely inhibited by the addition of small amounts of hydrochloric acid, the effect not being permanent if the acid is neutralised within a few minutes. Much greater concentrations of acid are required to render the surface of cobalt passive, for in this case the tendency for the formation of hydroxyl ions is much greater.

Alkali, either sodium or ammonium hydroxide, although speeding up the mutarotation, is without effect on the catalyst, the catalytic reaction proceeding at almost the same rate in alkaline as in pure aqueous solution.

The temperature coefficient of the catalytic reaction is doubled every five degrees, being almost the same as the temperature coefficient of the normal reaction. It is thus unlikely that the reaction occurs on the surface of the solid metal; for the temperature coefficient of such heterogeneous catalytic reactions rarely exceeds 1·3 per 10°. The acceleration of the mutarotation must therefore be due to a catalyst, present in the solution.

The published experimental data on the catalysis of the mutarotation of dextrose by hydroxyl ion are very conflicting. The concentrations of the hydroxyl ion are usually determined from hydrolysis and dissociation constants and the calculations are frequently subject to considerable errors. Asaka (*Zeitsch. physikal. Chem.*, 1900, **35**, 685) finds values for $\frac{K}{c_{OH}} \times 10^{-4}$, varying with the source of the hydroxyl ion; K is the velocity constant and $c_{OH'}$ the concentration of the hydroxyl ion. Some of the results are given below and it will be seen that the amounts of hydroxyl ion required to double the velocity constant in neutral solution vary between $1{\cdot}0 \times 10^{-4}$ and $1{\cdot}0 \times 10^{-6}$ N.

Source of OH′.	Temp.	$\frac{K}{c_{OH'}} \times 10^{-4}$.	[OH′] required to double K.	Author.
$NH_4{\cdot}OH$ NH_4Cl	25°	1·5	$1{\cdot}3 \times 10^{-6}$	Osaka.
Pyridine	,,	0·22	$9{\cdot}0 \times 10^{-6}$	,,
Aniline	,,	0·19	$10{\cdot}0 \times 10^{-6}$	,,
Na_2CO_3	20	0·0133	$1{\cdot}1 \times 10^{-4}$	Murschauser.*

* *Biochem. Zeitsch.*, 1920, **106**, 23.

The question now arises as to whether sufficient hydroxyl ion is produced by the metallic surface to account for the catalysis that is obtained. From Tables V and VI it will be observed that *N*/50,000 to *N*/100,000 acid is sufficient to inhibit the catalysis with metallic nickel, therefore the total amount of hydroxyl ion produced in the dextrose solution cannot be greater than corresponds with these concentrations of acids. These values are intermediate between the concentrations of Osaka and Murschauser, which were required to double the rate of mutarotation. We are thus unable to state definitely that the hydroxyl ion is the sole cause of the catalysis, but since the concentrations of hydroxyl ion produced in the polarimeter tube are of the same order as those found to be effective by Osaka, it would seem that this explanation of the catalysis is the most satisfactory that can be put forward.

EXPERIMENTAL.

Purity of Dextrose.—The catalytic activity of nickel is dependent on the purity of the dextrose and particularly on its acidity. Acid behaves as a negative catalyst even when the concentration present is insufficient to increase appreciably the rate of mutarotation. The greatest acceleration of the rate of mutarotation was given by a quantity of Kahlbaum's dextrose which was neutral to litmus. Dextrose, free from acid and crystallised many times from alcohol and water, usually gave a lower activity than this dextrose. Dextrose from several sources, purified in different ways, could always be catalysed to some extent by metallic nickel.

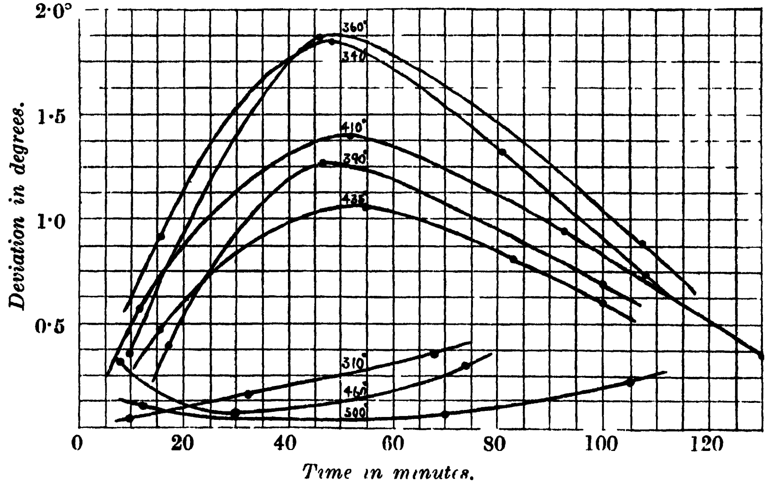
Purity of Nickel and Cobalt.—Nickel was used as foil and in the form of spheres. The former was a pure sheet nickel and the latter the pure metal supplied by the Mond Nickel Co. The surface of the metal was found to deteriorate with continued use, but its activity could be restored by cleaning with emery cloth. Different batches of the nickel spheres varied greatly in their behaviour on oxidation and reduction and in their activity. In some cases expansion of the nickel spheres occurred on oxidation and cracks frequently developed. These irregularities made the reproducibility of results somewhat difficult.

The magnitude of the effect with untreated metallic nickel was dependent on the manner of cleansing of the nickel surface; thus, when cleaned with alcohol and ether, the surface was more active than when cleaned with hydrochloric acid.

The cobalt contained traces of iron, but was free from nickel.

Apparatus.—The catalysis was carried out in polarimeter tubes, which were gently rocked on a platform between the polariser and the analyser by means of a crank and motor, and a constant rate of stirring was secured by means of a small opaque glass bead, which traversed the whole length of the tube. A constant temperature was maintained by circulating a stream of water at 25° through the outer jackets of the polarimeter tubes arranged in parallel. The activity of the nickel surface was found to be increased by a preliminary oxidation and reduction. It was necessary to standardise carefully the conditions under which the oxidation and reduction were carried out. Gas furnaces were first employed for both the oxidation and reduction, but in the majority of the experiments the reduction was effected in an electric furnace. The active material was employed in several forms. Thus in some cases tubes of foil closely fitting the internal surface of the polarimeter tube were employed as catalysts. Nickel spheres of about 0·4 cm. diameter and strips of metal were also used.

FIG. 1.



The readings were taken as rapidly as possible, by stopping the rocker and holding the tubes in position. The average time taken to read each tube was one minute.

Temperature of Reduction and the Activity of the Nickel.

Nickel spheres were oxidised in a nickel tube at approximately 800° for half an hour and then placed in a platinum boat and reduced at a constant rate of flow for one hour and cooled to 100° in electrolytic hydrogen. The electric furnace was suspended, so that it could be gently rocked during the operation.

The appearance of the nickel spheres after this treatment varied with the temperature of reduction; below 300° the surface was a dull grey, and above 340° it had a bright metallic appearance. The dull grey surface was rarely active. Kahlbaum's dextrose was employed throughout, and the concentration of the solution was 10 per cent. by weight of dextrose. This concentration was employed throughout the work. Twenty spheres of a total area of 3·2 sq. cm. were used in each 2-dcm. tube. The results are summarised in Table I and Fig. 1. The differences between the polarimeter readings of the blank and of the tube containing the nickel spheres are plotted against the time in minutes. The maximum difference between the two readings usually occurred at about forty-eight minutes if the spheres were appreciably active. The maximum deviations for each temperature of reduction are given in the table, and the appearance of the spheres is noted.

TABLE I.

Temp.	Maximum deviation.	Appearance.	Temp.	Maximum deviation.	Appearance.
500°	0·04°	Bright.	360°	1·88° *	Bright.
460	0·14	„	340	1·84 *	„
435	1·10	„	310	0·26	Dull.
410	1·42	„	200	unchanged	Black.
390	1·26	„			

* Effects of this magnitude were only produced with Kahlbaum's dextrose.

The maximum activity under these conditions is obtained by reduction at 340—360°.

Temperature Coefficient of Catalytic Reaction.

The catalytic action of nickel on dextrose solution was compared at two temperatures, 7° and 26°, and of cobalt at 3·8° and 26°. The two metal strips of equal surface area employed in each experiment were cut from the same sheet, and oxidised at the same temperature and reduced at 380°, side by side in the furnaces. The activity of the two strips was as nearly as possible the same. The temperature of the polarimeter tubes was maintained at the above values by streams of water through the outer jackets. The maximum deviation between the polarimeter readings of the blank experiment and the tube containing the metal was greatest for the lower of the two temperatures; thus a deviation of 1·46° at 7° against 0·87° at 26° occurred with the metallic nickel. These deviations are not a measure of the relative speeds of the reaction, as will be seen from the velocity constants over the first three-quarters of the reaction, given in Table II. The velocity constants are calculated from the formula, $K = \frac{1}{t} \log \frac{a}{a - x}$.

TABLE II.

Metal.	Temp.	Maximum deviation.	K Blank.	K Metal.	$\frac{K \text{ Metal}}{K \text{ Blank}}$
Nickel	7°	1·46°	0·00160	0·00226	1·41
,,	26°	0·87	0·0119	0·0173	1·45
Cobalt	3·8°	4·15	0·00134	0·00369	2·76
,,	26°	2·55	0·0124	0·0340	2·74

The ratio of $\frac{K \text{ metal}}{K \text{ blank}}$ is the same at the two temperatures, showing that in the cases of both nickel and cobalt the temperature coefficient of the catalytic reaction is almost identical with that of the normal reaction. The velocity constant is thus doubled for every 5° rise in temperature.

Deterioration of the Activity of the Surface.

The deterioration of the surface with time is mainly caused by the dissolution of the active metal. The nature of the effect can be seen from the following typical results.

The metal after use in one experiment was immediately washed with dextrose solution, transferred to a newly-made solution, and the rate of mutarotation determined. When nickel spheres were used, the activity of the metal was completely destroyed after use in one experiment, but with the more active nickel and cobalt strips, the metal still possessed residual activity. The following mean velocity constants for the first hour of the mutarotation illustrate this effect.

TABLE III.

No.	Temp.	Metal.	K.		K.
1.	25°	Nickel freshly reduced.	0·0144	used again.	0·0122
2.	25	Blank.	0·0114		0·0113
3.	27	Cobalt freshly reduced.	0·0245	used again.	0·0177
4.	27	Blank.	0·0122		0·0122

Since it was possible that the activity of the metal had been transferred to the solution, the liquid from a previous experiment was mixed with a freshly prepared solution of dextrose. When the spheres were used, the solution was frequently inactive, but occasionally the liquid itself contained active material, which was able to catalyse the speed of reaction of a fresh solution. Thus in the two experiments above, when 50 per cent. of the solution from (1) or (3) was added to a fresh dextrose solution, the rates of mutarotation were greater than when 50 per cent. of either of the solutions (2) and (4) was added to a fresh dextrose solution. From (1) $K = 0{\cdot}0129$, (2) $K = 0{\cdot}0113$, (3) $K = 0{\cdot}0153$ and (4) $K = 0{\cdot}0122$.

Kahlbaum's dextrose recovered by evaporation of the aqueous solution to dryness, gave the normal velocity of mutarotation, although it contained nickel.

The metal goes into solution as hydroxide, for both hydroxyl ions and the metal cations can be detected in the solutions. A freshly reduced cobalt surface is rapidly attacked by distilled water, liberating hydroxyl ions. The effect with untreated or oxidised cobalt is much smaller. The concentration of hydroxyl ions in the experiments with cobalt and dextrose was about $N/20{,}000$ at the end of the mutarotation, and this concentration is sufficiently great to account for the observed catalytic effect (Hudson, *J. Amer. Chem. Soc.*, 1907, **29**, 1574).

Nickel slowly gives hydroxyl ions with water, but no hydroxyl ions could be detected in the dextrose solutions by means of litmus, even in the middle of the experiments. Since the alkalinity of the dextrose solutions slowly decreases on keeping, it is probable that, in the case of nickel, hydroxyl ion is only present in the neighbourhood of the nickel surface.

The Effect of Dissolved Oxygen.

Since water containing oxygen attacks cobalt and nickel, it was possible that the oxygen dissolved from the air was responsible for the catalysis. Water was freed from oxygen and carbon dioxide by boiling, and saturated with hydrogen. When the water had cooled to the ordinary temperature, dextrose was introduced without admitting any air to the apparatus. The solution of dextrose was rapidly transferred to a polarimeter tube containing either reduced nickel or cobalt. At the same time, a dextrose solution was made up in distilled water saturated with air, and the effect of a strip of metal determined. The two strips were cut from the same sheet and were reduced side by side.

The catalysis was somewhat greater in the boiled solution than in the solution containing air, possibly owing to the removal of carbonic acid, which when present would reduce the hydroxyl-ion concentration. It is thus clear that the catalysis is not determined by the oxygen dissolved in the water.

Acidity and Alkalinity of the Dextrose Solution.

The addition of small quantities of sodium hydroxide or hydrochloric acid to the dextrose solutions yielded interesting results. The experiments are divided into two series, the first a preliminary series with nickel tubes and the second with nickel spheres, carried out after more experience had been gained. In the preliminary series sometimes new tubes and at other times the old tubes newly reduced were used. This was unsatisfactory, as the activity of the tubes changed with use. It was thus necessary to take the mean of the results. Acid was found to destroy the activity of the nickel, whereas alkali on the whole did not appear to decrease the catalytic effect. Since carbon dioxide was not removed from the solution, the alkali may have been present as carbonate, but at these dilutions the degree of hydrolysis is considerable. The maximum lead in degrees given by the nickel tube over the blank is given in Table IV. From the mean values the effect of the alkali is seen to be slight. The effect of continued use with alkaline dextrose solutions is seen in the last row of figures.

Ammonia appears to resemble sodium hydroxide in its action.

TABLE IV.

Effect of Alkali on the Catalysis.

Normality of NaOH.	Maximum load.	Mean,
None	1·4, 0·62, 0·95, 0·80	0·94
N/20,000	0·84	0·84
N/10,000	0·62, 0·76, 1·36, 0·75, 0·73	0·84
N/5000	0·87, 0·57, 1·01, 0·65	0·77
N/2500	1·03, 1·07, 0·86, 0·86	0·95
None *	0·50, 0·53, 0·28, 0·16	0·37

* Previously used with alkali.

It became evident that a nickel surface could only be used once if reproducibility of results was to be obtained. In the second series, it was therefore decided to use nickel spheres, since these could be replaced after every experiment and a large number could be oxidised and reduced at one time, under identical conditions. These spheres made possible comparative measurements with the same active surface of nickel, and experiments with acid and alkali could be carried out simultaneously. Four to six tubes were employed in each series of experiments, and a typical series contained the following experiments: (1) blank; (2) dextrose solution and twenty nickel spheres, 0·4 cm. in diameter; (3) dextrose solution and alkali; (4) dextrose solution, alkali, and nickel spheres; (5) dextrose solution and acid, and (6) dextrose solution, acid, and nickel spheres.

The magnitude of the catalytic effect varied with the different batches of spheres, and more difficulty was experienced in obtaining an active surface than with sheet nickel on account of the smaller area employed.

Concentrations of acid and alkali varying from *N*/1000 to *N*/500,000 were used. With alkali of greater concentration than *N*/1000, the speed of mutarotation was too great to be conveniently measured. The requisite quantity of acid or alkali was added as one drop of a solution of the necessary strength.

Results with Acid and Alkali.

The change in the velocity constants with time in some of the experiments is given in Table V. Where catalysis occurs, the velocity constants increase to a maximum value and then decrease.

TABLE V.

Acidity or alkalinity.	Velocity constant.	Mean *K* for the first hour.
Zero.	0·0104, 0·0093, 0·0097, 0·0101	0·0098
,, + Ni.	0·0109, 0·0120, 0·0140, 0·0112	0·0123
N/1000-HCl.	0·0097, 0·0104, 0·0091, 0·0088	0·0098
,, + Ni.	0·0093, 0·0100, 0·0094, 0·0084	0·0094
Zero.	0·0097, 0·0096, 0·0103	0·0097
,, + Ni.	0·0142, 0·0148, 0·0067	0·0145
N/10,000-NaOH.	0·0110, 0·0109, 0·0095	0·0110
,, + Ni.	0·0129, 0·0173, 0·0090	0·0150
N/10,000-HCl.	0·0111, 0·0102, 0·0094	0·0107
,, + Ni.	0·0109, 0·0106, 0·0080	0·0108

The mean velocity constant for Kahlbaum's dextrose was 0·0098. In a series of experiments with dextrose supplied by the British Drug Houses, Ltd., the mean velocity constant was 0·0101; the rates of mutarotation, therefore, are very similar.

In Table VI the differences between the mean velocity constant of the blank and that with nickel are given, together with the maximum deviation.

TABLE VI.

Nature of dextrose	Alkali and acid concentration.	Dextrose only. Δ.		Dextrose with alkali. Δ.		Dextrose with acid. Δ.	
		Vel. const.	Max. dev.	Vel. const.	Max. dev.	Vel. const.	Max. dev.
K.	*N*/1000	+ 0·0025	0·67°	—	—	– 0·0003	0·00°
K.	*N*/10,000	+ 0·0047	1·35	+ 0·040	0·72°	+ 0·0001	0·06
B.D.H.	,,	+ 0·0060	0·90	—	—	+ 0·0002	0·15
B.D.H.	*N*/50,000	+ 0·0032	0·69	+ 0·054	0·71	+ 0·0017	0·22
* B.D.H.	,,	+ 0·0057	0·78	—	—	+ 0·0002	0·06
B.D.H.	*N*/100,000	+ 0·0032	0·62	+ 0·028	0·50	+ 0·0003	0·25
B.D.H.	*N*/500,000	+ 0·0023	0·52	+ 0·010	0·23	+ 0·0006	0·15

* Nickel tubes.

The negative catalytic effect of hydrochloric acid is very marked up to a concentration of *N*/50,000; above this concentration up to *N*/500,000, the acid still reduces the activity of the nickel. On the other hand, alkali does not materially reduce the activity, except in the doubtful case of *N*/500,000-alkali.

More nickel is detected in the solution when hydrochloric acid is present.

Cobalt was much less sensitive to hydrochloric acid, *N*/10,000-acid being insufficient to destroy the catalysis. A slight initial retardation is noticed, but after a few minutes the catalytic reaction proceeds at its full rate.

Effect of Metals and their Oxides on the Mutarotation of Dextrose.

In order to compare the effects of various metals, a number of metal strips were placed in the polarimeter tubes, and stirring was effected by means of an oxidised nickel sphere. The copper and iron were oxidised at 800° for ten minutes and the cobalt and nickel for half an hour; the strips were all reduced at 380° for half an hour. The values for the velocity constant at 25° are given in Table VII. The areas of the metal strips were only approximately the same, and the amount of active reduced metal differed greatly in the four cases. Owing to the difficulty of oxidising metallic nickel, the amount of reduced metal was much smaller than in the cases of iron and cobalt. Also the best temperature of reduction may not be the same for other metals as for nickel.

TABLE VII.

Various Metals.

Metal.	Area in sq. cm.	Velocity constant. 16 min.	39 min.	62 min.	78 min.	1st hr.	Percentage of metal in the solution.
Fe	40	0·0137	0·0164	0·0157	0·0125	0·0152	Not determined.
Ni	24	0·0118	0·0128	0·0125	0·0135	0·0123	0·0076
Cu	39	0·0118	0·0126	0·0119	0·0117	0·0121	0·022
Co	35	0·0234	0·0400	0·0490	—	0·0361	0·0035
Blank		0·0119	0·0112	0·0118	0·0115	0·0116	—

The amount of metal which goes into solution is no criterion of the activity of the metal.

The oxidised metal was always less active than the reduced metal, and in the case of nickel the oxidised material was practically inactive. Two series of experiments are given below, one in which nickel and cobalt and the other in which nickel and copper are compared with one another. In each series the five tubes were compared simultaneously. The mean velocity constant for the first hour is given.

TABLE VIII.

Series.	Copper.	Nickel.	Cobalt.	Blank.
	Velocity constant.			
(1) Oxidised.	0·0113	0·0100	—	0·0100
(1) Reduced.	0·0174	0·0204	—	,,
(2) Oxidised.	—	0·0100	0·0145	,,
(2) Reduced.	—	0·0144	0·0297	,,

Nickel in these and in other experiments always gave a higher acceleration of the mutarotation than copper. Oxidised cobalt catalyses the mutarotation of dextrose at about the same speed as reduced nickel.

The nickel solutions in series (2) were acid to phenolphthalein, and both cobalt solutions were alkaline to this indicator. The alkalinity of the solution in contact with the reduced metal was *N*/6000, whereas that in contact with the oxidised metal was *N*/80,000.

Other Sugars.

The property possessed by nickel of catalysing the rate of mutarotation was found to extend to other sugars than dextrose. Only qualitative experiments were made.

Lactose. Maximum deviation of 0·48° on 4·15°, 0·20° on 2·51°, and 0·22° on 2·37°.

Maltose. 0·25° on 2·91°.

Lævulose. Slight effect.

Galactose. No effect.

Owing to the small quantities of maltose, lævulose, and galactose available, no great importance can be attached to these results. It, however, appears from the lactose experiments that the catalytic action of nickel also takes place with other sugars.

Summary.

Nickel, cobalt, iron, and copper have been shown to catalyse the mutarotation of dextrose. The metals are more active after a preliminary oxidation and reduction of the surface, and the temperature of reduction has an important bearing on the activity of the metal. An oxidised metal surface is either inactive or gives a much smaller catalytic effect than the reduced surface.

The surface of the catalyst deteriorates with time, owing to the dissolution of some of the metal as hydroxide.

The hydroxyl-ion concentration obtained is of the same order as that necessary to produce the observed change in the velocity of mutarotation. The catalytic reaction is not caused by the oxygen dissolved in the dextrose solution, for the catalysis occurs in oxygen-free water, but is presumably associated with the oxygen and hydrogen dissolved by or in combination with the metal.

Very low concentrations of acid inhibit the activity of nickel and reduce that of cobalt, whereas alkali has but a slight effect on the catalytic reaction.

The velocity constant of the catalytic reaction is doubled for every 5°; it is thus unlikely that the catalysis occurs on the surface of the metal.

In conclusion, we wish to express our thanks to Professor F. G. Donnan for providing the facilities for this work.

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CCXXII.—*The Decomposition of Ozone by Light of the Visible Spectrum.*

By Robert Owen Griffith and William James Shutt.

The photochemical decomposition of ozone has been studied by Regener (*Ann. Physik*, 1906, [iv], **20**, 1033), von Bahr (*ibid.*, 1910, [iv], **33**, 598) and Weigert (*Zeitsch. physikal. Chem.*, 1912, **80**, 78). All these investigators employed ultra-violet light, the effective deozonising region being in the neighbourhood of 254 $\mu\mu$. It is also known that, in the presence of chlorine (compare Weigert, *Zeitsch. Elektrochem.*, 1908, **14**, 591), light of longer wave-length, namely, that of the blue and violet portions of the spectrum, will cause ozone to decompose. The object of this investigation was to test, in a purely qualitative manner, whether ozone is decomposed by the action of light of still longer wave-length, that of 500 to 800 $\mu\mu$. In the general discussion on catalysis before the Faraday Society, September, 1921, W. C. McC. Lewis has shown, from theoretical considerations based on his radiation theory of chemical reactivity, that the longest wave-length of light capable of decomposing ozone in a unimolecular manner should be about 700 $\mu\mu$. This, however, does not eliminate the possibility that shorter waves, in addition, may have the same effect. The results of this preliminary work seem to prove that ozone decomposes under the action of red and yellow light; but it is hoped, at a later date, to define the limits of the effective spectral regions with greater precision than is now possible.

EXPERIMENTAL.

The method adopted to ascertain whether photochemical decomposition of ozone occurs on illumination with light of the visible portion of the spectrum was that of following the pressure changes which take place when a constant volume of ozonised oxygen is subjected to light of constant intensity. Since two volumes of ozone are converted, when decomposed, into three volumes of oxygen, the extent of the decomposition may be calculated.

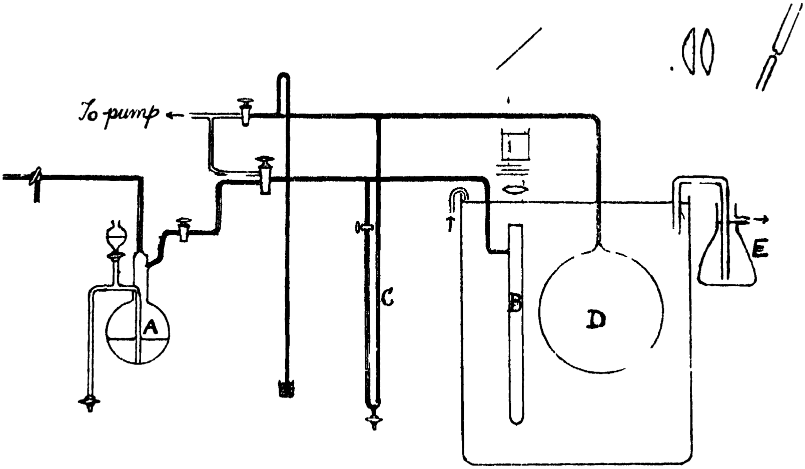
Ozone was prepared by the method of Fischer and Massenez (*Zeitsch. anorg. Chem.*, 1907, **52**, 202, 229), namely, the electrolysis of dilute sulphuric acid at a high anodic current density, using a water-cooled platinum anode. This was made by shaping a thin platinum tube of 3½ mm. external diameter into the form of a **U**, the two vertical limbs being about 5 cm. in length, the horizontal portion 3 cm. The two ends were silver-soldered into two stout copper tubes. The horizontal portion of the anode was sealed into blue enamel glass, which was then carefully filed down at one side so as to expose a platinum surface of 6 × 0·5 sq. mm., and the remainder of the tube was given several coats of paraffin wax. The anode was placed in the central limb of a double H vessel, the two outer limbs of which contained lead cathodes, and the horizontal connecting portions glass wool. Cooling was effected by a stream of water (temperature 8—10°) flowing through the platinum tube, the velocity being maintained at about 1·5 litres per minute, and also by immersion of the whole cell in a bath at the same temperature.

Using, as recommended by Fischer and Massenez (*loc. cit.*), an acid of density 1·085 as electrolyte and an anodic current density of approximately 45 amperes per sq. cm., corresponding with a current of 1·3 amperes, no difficulty was experienced in obtaining an ozone concentration of 17 per cent. by weight (11 per cent. by volume). The ozonised oxygen rising from the anode was collected in a small glass bell and conveyed, by capillary tubing, either to a reservoir in which it could be stored over concentrated sulphuric acid or through an absorption tube for analysis. From time to time the gas given by this apparatus was analysed and was found to be of almost unchanged composition, 16·8 to 17·1 per cent. of ozone.* This was the concentration of ozone employed in most of the experiments to be described.

The remainder of the apparatus is shown in the figure.

From the gas reservoir, *A*, the ozone was transferred to the experimental tube, *B*, of dimensions 40 cm. in length, 1·8 cm. in diameter, and capacity 107 c.c., which stood vertically in a glass thermostat. The sulphuric acid manometer, *C*, made of capillary tubing of 1 mm. bore, was connected as shown with the tube, *B*, and the compensator, *D*, a glass balloon of 1 litre capacity, immersed in the thermostat. Finally, the whole apparatus was joined to mercury- and water-pumps, through a tube containing potassium hydroxide, which served the purpose of decomposing the ozone as

FIG. 1.



it was pumped out, thereby preventing its attacking the mercury of the pump. The apparatus was constructed entirely of glass, and the gas came into contact only with glass, sulphuric acid, and, to a slight extent, with glacial phosphoric acid used for lubricating the taps. Before being sealed to the rest of the apparatus, the reaction tube, *B*, was treated with chromic acid mixture, rinsed with distilled water, and dried, care being taken to exclude particles of dust. This was rendered necessary since Warburg (*Ann. Physik*, 1902, [iv], 9, 1286) found that ozone decomposes very slowly at the ordinary temperature in the dark, but that the rate may be much increased by traces of foreign matter, which acts catalytically in promoting the unimolecular reaction $O_3 \longrightarrow O_2 + O$. He showed that the velocity of deozonisation is apparently independent of the nature of the agent used to dry the gas and that, in the tubes most free from dust particles, the ozone concentration fell only from 8 per cent. to 7·5 per cent. in the first 100 hours, at room temperature. Experiments carried out with the tube *B*, whilst showing a greater decomposition than this, proved that the amount of "catalytic dark decomposition," in all cases, was too small to affect the results obtained during the time the tube was illuminated. Thus the maximum "dark decomposition" ever observed corresponded with an increase of pressure of 5·4 mm. of sulphuric acid in 220 minutes. This maximum, which was far higher than the average amount of "dark decomposition," corresponds with a quantity approaching the order of the experimental error in reading the manometer, when reduced to the time taken for an experiment in which the tube was illuminated. Weigert (*loc. cit.*), in an investigation on the decomposition of ozone by ultra-violet light, observed a much greater decomposition in the dark, but this is probably due to the fact that his ozone was in contact with paraffin and also with sulphuric acid.

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* At a late stage in the work, damage to the anode necessitated the making of a new and possibly less efficient one. This, together with a higher temperature of the water used for cooling, resulted in a lower ozone concentration—13 per cent.—and a few experiments were made with this ozone.

The source of illumination used was a hand-regulated carbon arc projection lamp, consuming 30—35 amperes. The horizontal beam formed by two lenses was reflected vertically downwards by a plane mirror. It then passed through a layer of water, the thickness of which could be varied, two thick plates of crown glass (total thickness 3·2 cm.) and a double convex lens. Before entering the experimental tube it traversed a further layer of water, the depth of which could be adjusted by altering the level of the syphon, *E*. The intensity of the light of the carbon arc leaves much to be desired in point of constancy and, as a source of illumination for photochemical work in general, it is not very suitable; but, as the main purpose of this investigation was to establish qualitatively the decomposition of ozone in visible light, this disadvantage was outweighed by the strong intensity obtainable. By observing certain precautions, however, such as carefully regulating the distance between the poles so as to maintain a constant current strength, it was found possible to avoid large and sudden irregularities in the intensity of the light, but it is difficult to remedy the gradual change in the light due to movement of the position of the positive crater. During an experiment, a vigorous stream of water, either direct from the town supply or from an auxiliary thermostat, was passed through the main thermostat in order to maintain a constant temperature in the reaction tube. The temperatures employed in different experiments varied between 8° and 30°.

When the tube containing 16—17 per cent. of ozone at atmospheric pressure was illuminated, the beam appeared of a slight but distinct blue colour, indicating absorption of the less refrangible portion of the spectrum. This has previously been observed by several workers, among whom mention may be made of Liveing and Dewar (*Phil. Mag.*, 1888, [v], **25**, 286), although they state that the absorption bands of ozone in the visible part of the spectrum are extremely faint.

On exposure of the experimental tube containing ozone to light, the following changes in the pressure were observed. The pressure first increased rapidly for about fifteen seconds, then rose steadily, but more slowly; finally, on cutting off the light, the pressure fell, attaining in four minutes a constant value, which corresponded with a certain amount of decomposition of ozone. This result is due to a heating effect caused by absorption by the ozone of certain parts of the visible spectrum, the energy of which is converted into infra-red radiation. By the use of a light of constant intensity, after fifteen to twenty seconds, a stationary thermal state is reached when the amount of heat flowing out from the tube to the thermostat, maintained at constant temperature, is equal to that being generated by the absorption. The further, slower increase of pressure is that due to decomposition of ozone. When the light is turned off, the pressure again decreases as the temperature of the contents of the tube falls to that of the thermostat. Thus, in one experiment, the following figures were obtained:

Temperature of thermostat = 10°. Barometric pressure = 758 mm. Manometric difference at the start, 1·6 mm. of sulphuric acid. Manometric difference after five minutes' illumination, 20·4 mm. of sulphuric acid.

The light was then cut off and the manometer read after the lapse of a further five minutes.

Final manometric difference, 9·3 mm. of sulphuric acid. We therefore obtain as the increase of pressure due to decomposition of ozone during illumination for five minutes, 9·3 − 1·6 = 7·7 mm. of sulphuric acid, and an increase of pressure due to heating of the ozone, 20·4 − 9·3 = 11·1 mm. of sulphuric acid.

From the latter increase of pressure may be calculated the average rise of temperature in the tube. In this case the value obtained is 0·5°.

Table I shows one series of results out of many obtained by illuminating the experimental tube for successive intervals of five minutes and interpreting the observed manometric differences in the manner indicated in the above calculation.

TABLE I.

Temperature = 10°. Pressure = 768 mm. Ozone concentration = 11 per cent. by volume.

p_0.	p.	$p - p_0$.	p'.	$p' - p$.	ΔT.
1·7	13·4	11·7	29·3	15·9	0·79°
13·4	23·2	9·8	34·2	11·0	0·55
23·2	31·2	8·0	41·5	10·3	0·52
34·8	41·7	6·9	53·6	11·9	0·59
41·7	49·9	8·2	62·4	12·5	0·62
50·3	57·8	7·5	68·8	11·0	0·55

Where p_0 = the initial difference of pressure, before illumination, in mm. of sulphuric acid; p = the final difference of pressure after attainment of thermal equilibrium; p' = the difference of pressure immediately before cutting off the light; ΔT = the mean rise of temperature of the gas above the temperature of the thermostat.

The increase of pressure (column $p - p_0$) corresponding with total decomposition of the ozone present = 317 mm. of sulphuric acid.

These results show that, with the light employed, ozone undergoes decomposition and that the extent of decomposition, in equal intervals of time, is as nearly constant as could be anticipated from the nature of the source of the light.

In all our experiments in which decomposition of ozone was indicated, this heating effect (column ΔT) was observed. Its extent depended on the intensity of the light, but was usually of the order of 0·5°. This was the average rise of temperature of the ozonised oxygen during illumination, and it is, of course, in itself insufficient to account for the observed rate of decomposition. The possibility remained, however, that the gas near the centre of the tube might be at a far higher temperature, sufficiently high, in fact, to account for the decomposition by the bimolecular, thermal reaction $2O_3 \longrightarrow 3O_2$, which has been studied by Warburg (*loc. cit.*), Clement (*Ann. Physik*, 1904, [iv], **14**, 342), and Chapman and Jones (T., 1910, **97**, 2463). That this, in all probability, is not so may be shown in the following way. During illumination the gas is heated owing to the absorption of light, the outside of the tube is maintained at a constant temperature, and the internal temperature increases from T_0, at the outside, to T_{max}, the temperature at the centre. As only a small fraction of the light is absorbed, we may consider that the intensities of the incident and emergent beams are practically identical and therefore (with constant intensity of light) the temperature at any point of the tube is dependent only on the distance from the axis and is independent of the distance from the ends. Also consider that the whole cross-section of the tube is illuminated at equal intensity, that no convection occurs, and that heat flows only at right angles to the length of the tube. With these assumptions, it can readily be shown that the maximum rise of temperature is double the mean rise. This is necessarily the highest temperature which the hottest part of the gas can attain, as convection, which undoubtedly occurs, tends to decrease this value. The largest mean rise of temperature observed in these experiments amounted to 0·8° (see Table I), and thus the maximum rise was, at the most, double this or 1·6°. It may be calculated from Warburg's results for the rates of the bimolecular decomposition of ozone at different temperatures that in order to account for the observed velocity of deozonisation in this experiment, the whole of the gas would have to be at a temperature between 80° and 90°. It is therefore entirely justifiable to assume that the slight warming which the gas undergoes on illumination is not the cause of its decomposition, and that the latter is due to the light employed.

As stated above, the beam from the carbon arc passed through several thicknesses of glass and through a layer of water before entering the ozonised oxygen, in order that most of the ultra-violet and infra-red portions of the spectrum might be removed. By means of photographs taken on a Hilger quartz spectrograph, it was found that the glass screens deprived the beam of light from the arc of all that portion of the spectrum of wave-lengths shorter than 330 $\mu\mu$.* The conclusion that ultra-violet light is not responsible for the photochemical decomposition of ozone observed in these experiments is further supported by the fact that the rate of decomposition was not sensibly diminished by interposition, between the source of the light and the tube, of an æsculin filter, which transmitted only wave-lengths longer than 380 $\mu\mu$.

The other limit to the wave-length of the effective light entering the experimental tube is obtained from a consideration of the absorption of water in the extreme red portion of the visible spectrum. According to Nicholls (*Physical Rev.*, 1894, **1**, 1), the value of the absorption coefficient α for water is 0·272 at 779 $\mu\mu$, and this increases with increasing wave-length. The absorption coefficient is defined by the equation

$$I = I_0 e^{-\alpha d}.$$

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* For his kindness in taking these photographs, we have to thank Mr. L. W. Codd.

in which I_0 = the intensity of incident light of a given wave-length.
I = the intensity of emergent light of the same wave-length.
d = the thickness of the water layer in centimetres.

It follows, from Nicholls's value, that the fraction of light of wave-length 779 $\mu\mu$ transmitted through a layer of water 1 cm. in thickness is 0·76 and that through 10 cm. of water only 0·066. Hence, if wave-lengths of this order were effecting the decomposition of ozone, it would be anticipated that the rate of decomposition would vary with the thickness of the water screen through which the light passed. Experiments undertaken to test this point showed that no such effect was produced. The results of two such experiments, in which the times of illumination were five minutes, are given in Table II.

TABLE II.

	Thickness of water layer.	p_0.	p.	$p - p_0$.
Expt. I.	1 cm.	1·5	5·0	3·5
	10 „	5·0	8·3	3·3
Expt. II.	1 „	13·2	19·9	6·7
	10 „	19·9	25·6	5·7

Within the experimental error, the rates of decomposition are independent of the thickness of the water screen, and, in consequence, it may be assumed that light of wave-length longer than 770 $\mu\mu$ was not causing the decomposition of ozone in these experiments.

We therefore draw the conclusion that light of wave-lengths between 400 $\mu\mu$ and 780 $\mu\mu$, that is, light of the visible portion of the spectrum, is capable of decomposing ozone.

The problem of further narrowing the effective limits of the spectrum presented some difficulty. Filters of aqueous solutions of inorganic salts were examined, but were found, in most cases, to be useless, as either the limits of transmission were not definite enough or, where the selection was better, the light transmitted was too feeble to effect any decomposition during a convenient interval of time. The filters finally employed were gelatin film filters obtained from Messrs. Kodak, Ltd., the percentage transmission of each filter, at a given wave-length, being taken from tables supplied by the makers. It was not possible to verify these figures, as a spectrophotometer was not available; the limits of visible transmission, however, were checked, for each filter, on a Hilger wave-length spectrometer and were found to agree with what would be anticipated from the maker's tables. Each filter was mounted between glass plates and placed so as to permit cooling by the water flowing around and over the experimental tube.

The method of working was as follows. The amount of decomposition of ozone produced in a given time by light transmitted through one of the filters was compared with that effected, in the same time, by white light of the same intensity. As the intensity of the light tended to be variable, this comparison was made on the results of three successive experiments; in the first and the third white light was used, and in the second the filter was interposed. The amount of decomposition registered manometrically in the second experiment was compared with the mean of the other two. Experiments in which the results of the first and the third varied by more than 40 per cent. of the larger reading were rejected. The results obtained in this manner are shown in Table III.

TABLE III.

Percentage decomposition of ozone.

	Filter A.	Filter B.	Filter C.*	Filter D.	Filter E.*
	17	24	40	70	10
	22	25	44	86	
	20	32		85	
		37		71	
		39		71	
		36		88	
		42		85	
		37		73	
				76	
Mean	20	34	42	78	10

* The transmissive power of these filters was affected by the strong light employed and, in consequence, no further experiments could be carried out with them.

The figures in the table are percentage decompositions effected by light transmitted through the corresponding filters compared with that caused by white light of the same intensity, under the same conditions. Table IV gives the percentage transmissions of these filters at various wave-lengths as determined by the makers, Messrs. Kodak, Ltd., and published in their booklet "Wratten Light Filters."

From the figures given in Tables III and IV the following conclusions may be drawn.

(1) Light of the extreme red portion of the visible spectrum is capable of decomposing ozone. The head of this active band must lie between 670 and 760 $\mu\mu$, since light transmitted through filter A effects 20 per cent. of the decomposition caused by the whole of the visible spectrum and it is only at wave-lengths longer than

TABLE IV.

Wave-length. μμ.	Filter A. (70).	Filter B. (29).	Filter C. (32).	Filter D. (12).	Filter E. (43).*
400			49·0		63·2
490			20·2	0·3	54·0
510			4·0	28·0	50·0
590			Nil.	87·0	1·0
600			6·4	88·0	
610		0·4	34·0	89·0	
620		13·8	63·0	89·0	
650	0·4	63·6	73·0	91·0	
670	19·6	69·0	70·0	92·0	
680	34·0	70·0	68·0	93·0	
700	45·5	71·5	65·0	94·0	

* The numbers in brackets at the heads of the columns of percentage transmissions are the makers' numbers for the filters.

670 μμ that the transmission reaches 20 per cent. The effect of interposition of this filter was examined with especial care, and experiments with it were carried out over time intervals longer than five minutes, in one case above half an hour. In all cases the extent of decomposition was found to be approximately proportional to the time of exposure and about 20 per cent. of that observed with white light.

(2) Light of wave-lengths between 615 and 510 μμ is effective in causing decomposition of ozone. It is considered improbable that light of wave-lengths between 670 and 615 μμ is causing deozonisation, since the decomposition obtained by the use of filter B, which transmits in this region, is only so much in excess of that obtained with filter A, as would be expected from its (B's) increased transmission of light of wave-length longer than 670 μμ. The high percentage decomposition obtained with light transmitted through filter D indicates that a second band of light is also causing deozonisation, since the light present of wave-length longer than 670 μμ is now insufficient to account for the observed result. The average transmissions of filters A and D to light of wave-lengths between 670 and 700 μμ are in the ratio of 40 to 90, whereas the percentage decompositions observed with each are in the ratio of 20 to 78. The limit of 510 μμ is set to one end of this active band by the low transmission of filter D to shorter waves than those of this value. The other end of the band is defined by the results obtained with filter C. Light transmitted by this filter effects a slightly greater percentage decomposition than that transmitted by filter B, although the latter allows more light of wave-lengths longer than 670 μμ to pass through. It may be inferred from this result that part of the second active band is transmitted by

filter C, but is absorbed by filter B. Hence it follows that the longer limit of this band must lie between 620 and 610 $\mu\mu$.

(3) As regards the effect of the remaining portion of the visible spectrum, namely, that of wave-lengths between 400 and 510 $\mu\mu$, no definite inference can be drawn from the data. The use of filter E, which transmits in this region, is accompanied by a small decomposition of the ozone. Since, however, this filter transmits 10 per cent. of the energy of the incident light of wave-length 550 $\mu\mu$, and more of that of shorter wave-lengths, it is possible to account for the observed decomposition by assuming it to be due to light of wave-lengths between 550 and 520 $\mu\mu$, which is also transmitted by filter D. Consequently we incline to the opinion that if light of wave-lengths between 510 and 400 $\mu\mu$ is capable of causing deozonisation, its activity is very small in comparison with that of either of the two active regions already discussed, namely, 760 to 670 $\mu\mu$ and 615 to 510 $\mu\mu$.

Discussion of Results.

We may compare the results given above for the photochemically active portions of the visible spectrum with the absorption spectrum of ozone, which has been determined by Chappuis (*Compt. rend.*, 1880, **91**, 985; 1882, **94**, 858), Ladenburg and Lehmann (*Ber. Deut. physikal. Ges.*, 1906, **4**, 125) and others. Chappuis employed a tube containing ozonised oxygen, prepared by the silent discharge method, and found eleven absorption bands in the visible region. The band of longest wave-length was located at 629 $\mu\mu$, and the two most intense on either side of the sodium line, the one between 609·5 and 593·5 $\mu\mu$, the other between 577 and 560 $\mu\mu$. Both the characteristic bands are also shown by the blue liquid ozone. Of the bands found by Chappuis, four, including the two most intense, lie in the region between 520 and 615 $\mu\mu$, which has been found by us to be one of the regions effective in causing decomposition of ozone. As regards the relative effectiveness of the light at each of these four bands, nothing can be said at present. It may be that the light energy of wave-length corresponding with one of the bands alone is used in activating the ozone molecule, that of the others being converted into heat, or it may be that all the bands contribute, to some extent, to the decomposition. Luther (*Zeitsch. Elektrochem.*, 1908, **14**, 447) has expressed the opinion that in photochemical reaction all the absorbed wave-lengths are chemically effective, but, in many cases, the results are not noticeable.

No absorption bands appear to have been found for ozone in the region of wave-lengths 760 to 670 $\mu\mu$, which has been found by us to be photochemically active. However, Ladenburg and Lehmann (*loc. cit.*), using a gas containing a very high percentage of ozone, prepared by the Goldstein (E. Goldstein, *Ber.*, 1903, **36**, 3042) method, found, in addition to the bands observed by Chappuis, "general" absorption extending over the region of wave-lengths longer than 500 μμ. It therefore seems probable that the photochemically effective portion of the spectrum between 670 and 760 μμ lies in this region of "general" absorption.

Summary.

1. The action of light of the visible spectrum on ozone has been investigated.
2. At room temperature, ozonised oxygen, containing 16 per cent. (by weight) of ozone, is deozonised by the action of intense light of wave-lengths between 400 and 800 μμ.
3. Reasons are given to show that the slight heating which the gas undergoes is not the cause of the decomposition.
4. The use of light filters indicates that the effective regions of the spectrum lie between (*a*) 760 and 670 μμ and (*b*) 615 and 510 μμ.

In conclusion, we desire to express our thanks to Professor W. C. McC. Lewis, who suggested this work, for advice during its course.

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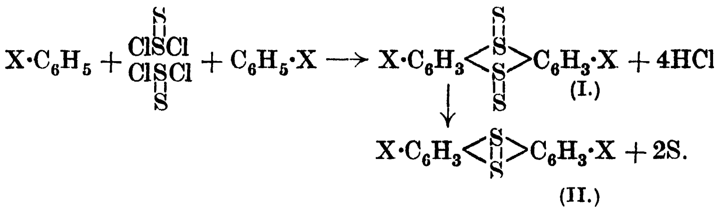
CCXXIII.—*Syntheses in the Thianthren Series. Part I.*

By JÑANENDRA NATH RÂY.

THE present investigation was undertaken with two objects in view, first, to ascertain the extent of the applicability of aluminium amalgam as a condensing agent, and, secondly, to develop a convenient method of synthesising thianthren derivatives, which appear to have been very little investigated. Fries and Engelbertz (*Annalen*, 1915, **407**, 194) failed to prepare dimethoxythianthren directly, which, however, was obtained from the corresponding diazosulphide by heating. Such a procedure is undoubtedly tedious, and therefore a systematic investigation seemed desirable.

Cohen (T., 1899, **75**, 887) condensed sulphur chloride with benzene and toluene by means of the aluminium–mercury couple, but in the case of the higher hydrocarbons the products were uncrystallisable oils which decomposed on distillation. In the present paper, compounds containing acetylamino-, chloro-, methyl, nitro-, nitroacetylamino-, acid chloride, keto-, and aldehydo-groups are described. It has been found that the reaction is inhibited by a nitro-group in the molecule, as no products could be isolated either under ordinary conditions or at high temperatures. The reaction with an iodo-compound is an interesting one, and will be dealt with subsequently. Usually, two molecules of sulphur chloride react with two molecules of the substance. Since the ortho-position of the sulphur atoms in thianthren has been proved (Deuss, *Ber.*, 1908, **41**, 2329), the reaction may be assumed to take place thus:



$$X{\cdot}C_6H_5 + \begin{matrix}S\\ \|\\ ClSCl\\ ClSCl\\ \|\\ S\end{matrix} + C_6H_5{\cdot}X \longrightarrow X{\cdot}C_6H_3{<}\begin{matrix}S\\ \|\\ S\\ S\\ \|\\ S\end{matrix}{>}C_6H_3{\cdot}X + 4HCl \quad \text{(I.)}$$

$$\downarrow$$

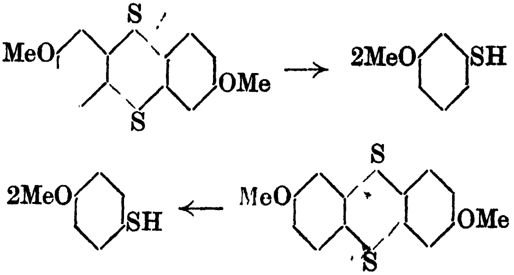
$$X{\cdot}C_6H_3{<}\begin{matrix}S\\ S\end{matrix}{>}C_6H_3{\cdot}X + 2S \quad \text{(II.)}$$

The intermediate compound (I) has actually been isolated. It is very unstable and suffers decomposition with moisture, liberating free sulphur. This compound is coloured, but on decomposition into the thianthren derivative the intensity diminishes and the product is only slightly coloured. These compounds all develop an intense coloration with sulphuric acid, which is discharged on dilution with the precipitation of the compound. Evidently, a sulphonium salt analogous to the intermediate compound I is formed (compare Fries and Volk, *Ber.*, 1909, **42**, 1170).

From acetanilide, diacetylaminothianthren was formed, from which the free amine was prepared by hydrolysis. This amine was diazotised and the product coupled with a few phenols and naphthols, but the dyes obtained showed no distinctive advantage over the corresponding benzene derivatives. This subject will be dealt with in a subsequent paper.

It was found in the course of this investigation that condensation between a hydrocarbon and an acid chloride cannot be effected by aluminium amalgam and that this catalyst is without action on acid chlorides. Therefore, it has been possible to condense benzoyl chloride with sulphur chloride, and the corresponding acid chloride of thianthrendicarboxylic acid has been isolated as the product.

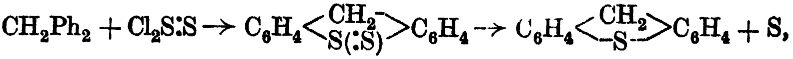
Phenolic ethers do not suffer hydrolysis, as with aluminium chloride, but the product of condensation in the case of anisole is an uncrystallisable oil. This oil gives the characteristic coloration with sulphuric acid, but breaks down into a mixture of two mercaptans on distillation. This behaviour has been found to be general in the series (compare Cohen, *loc. cit.*). Thus, in the case of anisole,



the decomposition products afford a clue to the constitution of the thianthren derivative.

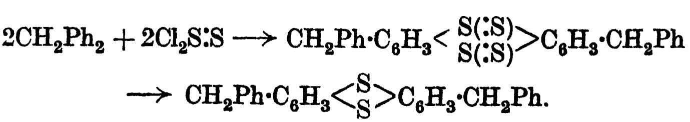
In the case of iodobenzene, complete separation of iodine takes place on mixing the constituents in the presence of the catalyst, but without it, iodine is not liberated even after boiling for many hours. Thianthren is isolated in small yield, but the greater part of the material is resinified.

Sulphur chloride was condensed with diphenylmethane in the expectation of getting thioxanthen,



$$CH_2Ph_2 + Cl_2S{:}S \rightarrow C_6H_4{<}\substack{CH_2-\\S(:S)}{>}C_6H_4 \rightarrow C_6H_4{<}\substack{CH_2\\-S-}{>}C_6H_4 + S,$$

but the corresponding dibenzylthianthren was obtained instead :



$$2CH_2Ph_2 + 2Cl_2S{:}S \longrightarrow CH_2Ph{\cdot}C_6H_3{<}\substack{S(:S)\\S(:S)}{>}C_6H_3{\cdot}CH_2Ph$$
$$\longrightarrow CH_2Ph{\cdot}C_6H_3{<}\substack{S\\S}{>}C_6H_3{\cdot}CH_2Ph.$$

It may be pointed out that the unsymmetrical constitution of sulphur chloride is demonstrated by the formation of thianthren (a compound of settled constitution) from benzene and sulphur chloride, for without the assumption of complicated tautomerism and rearrangement in the molecule the reaction can be explained in no other way than that depicted in this paper. Böeseken and Koning (*Rec. trav. chim.*, 1911, **30**, 116) studied the behaviour of sulphur chloride in the presence of aluminium chloride to ascertain its constitution, but they drew the conclusion that a clear picture of the reaction is impossible owing to its being obscured by side-reactions. The reaction in the presence of the aluminium-mercury couple is, however, a simple one (Cohen, *loc. cit.*), uninfluenced by concurrent reactions, and therefore the isolation of thianthren as the principal product is strong evidence in favour of the unsymmetrical constitution of sulphur chloride.

Böeseken and Koning (*loc. cit.*) found that *pp'*-dichlorodiphenyl sulphide and disulphide are the products of the reaction between chlorobenzene and sulphur chloride. The product in the present investigation is dichlorothianthren. Evidently, an entirely different course of reaction is induced by the two catalysts, aluminium chloride and aluminium amalgam.

EXPERIMENTAL.

The method of condensation was as follows. The substance was dissolved in dry carbon disulphide in a flask attached to a reflux condenser, through the upper end of which the sulphur chloride, dissolved in the same solvent, was added drop by drop. The catalyst, prepared from aluminium foil and dried between filter-paper, was quickly inserted into the flask before the addition of the sulphur chloride. The flask was cooled, when necessary, by immersion in water.

Condensation with Chlorobenzene: Dichlorothianthren.

A violent reaction ensued, and a bluish-green solid eventually separated when 10 c.c. of chlorobenzene, the couple prepared from 0·3 gram of aluminium, and 8 c.c. of sulphur chloride interacted in the presence of about 10 c.c. of carbon disulphide as diluent. After remaining for two hours, the mixture was warmed at 40° for two hours, and then decanted from the amalgam on to crushed ice. The product was collected, crystallised from glacial acetic acid, the crystals were dissolved in benzene and refluxed with copper powder to remove traces of sulphur, and the substance was finally twice crystallised from acetic acid, when it was obtained in needles, melting at 147°. It gave a bluish-violet coloration with sulphuric acid (Found: $Cl = 25{\cdot}7$; $S = 22{\cdot}98$. Calc., $Cl = 24{\cdot}99$; $S = 22{\cdot}4$ per cent.). Fries and Volk (*Annalen*, 1911, **381**, 312) gave 171° as the m. p. of 4 : 4'-dichlorothianthren, and their compound developed a deep blue colour with sulphuric acid. Possibly this compound is an isomeride.

Oxidation.—One gram of the substance was dissolved in glacial acetic acid and oxidised with boiling chromic acid mixture. The product was separated in the usual way. The sulphone crystallised from hot dilute acetic acid in needles, m. p. above 225° (Found: $S = 18{\cdot}5$. $C_{12}H_6O_4Cl_2S_2$ requires $S = 18{\cdot}3$ per cent.

Isolation of the Intermediate Compound.—The bluish-green solid separating from the reaction mixture was filtered and repeatedly washed with carbon disulphide, moisture being excluded. It was dried by pressing on a clean porous plate (Found: S = 37·2. $C_{12}H_6Cl_2S_4$ requires S = 36·6 per cent.).

Dichlorodimethylthianthren.

o-Chlorotoluene (5 c.c.) was condensed with 3·5 c.c. of sulphur chloride diluted with 10 c.c. of carbon disulphide. The reaction was instantaneous, and a greenish-black colour developed. The reaction was allowed to proceed at the ordinary temperature for two hours, the mixture was then heated on the water-bath for an hour, the product poured on crushed ice, and the reddish-brown, viscous mass extracted with boiling acetic acid containing a trace of water. The compound, which crystallised from the cold filtrate, was freed from sulphur by copper powder, and was dissolved in the minimum amount of chloroform and precipitated by pouring the solution into alcohol. After being then twice crystallised from acetic acid, it melted at 145° and developed a beautiful emerald-green coloration with sulphuric acid, which changed to blue on keeping (Found: Cl = 22·41; S = 21·0. $C_{14}H_{10}Cl_2S_2$ requires Cl = 22·68; S = 20·44 per cent.).

Oxidation with Nitric Acid: Preparation of the Sulphone.—The substance was heated on the water-bath with nitric acid and precipitated by water. The precipitate was crystallised from a boiling mixture of water and acetic acid. The sulphone melts and decomposes at a high temperature (Found: S = 16·85. Calc., S = 16·99 per cent.).

4 : 5-*Dichloro*-1 : 8-*dimethylthianthren.*

p-Chlorotoluene (5 c.c.) was condensed with 3·1 c.c. of sulphur chloride diluted with 10 c.c. of carbon disulphide, the reaction being moderated by cooling; eventually a greenish-black solid was produced. The reaction was allowed to proceed at the room temperature for two hours. When it slackened, the mixture was heated on the water-bath for an hour, and the product decomposed with crushed ice. The white solid thus obtained was crystallised from boiling xylene and freed from sulphur in the usual way. The substance is only slightly soluble in xylene, chloroform, acetone, or ether. It melts at 195—197°, and does not develop a coloration with sulphuric acid, probably owing to steric hindrance, as the positions 1, 4, 5, and 8 contiguous to the sulphur atoms are occupied

(Found: Cl = 22·39; S = 20·90. $C_{14}H_{10}Cl_2S_2$ requires Cl = 22·68; S = 20·44 per cent.).

The sulphone obtained on oxidation with nitric acid melts and decomposes above 250°.

Condensation of α-Chloronaphthalene and Sulphur Chloride.

α-Chloronaphthalene (2 c.c.) was condensed with 2 c.c. of sulphur chloride, and the product treated in the usual way. The resulting compound was crystallised from boiling glacial acetic acid containing a few drops of water. It melted at 64° (Found: Cl = 18·2; S = 17·2. $C_{20}H_{10}Cl_2S_2$ requires Cl = 18·4; S = 16·6 per cent.).

Diacetylaminothianthren.

Ten grams of acetanilide dissolved in 15 c.c. of carbon disulphide were treated with the calculated amount of sulphur chloride (2 mols.). The reaction was started by heating on the water-bath and the mixture boiled for four hours until the reaction was completed. The product, isolated in the usual way, was crystallised from boiling alcohol and from boiling dilute acetic acid until it was pure, when it melted at 198—200°. This compound gave a buff coloration with sulphuric acid (Found: N = 8·56; S = 19·8. $C_{16}H_{14}O_2N_2S_2$ requires N = 8·48; S = 19·39 per cent.).

The acetyl compound was hydrolysed with hydrochloric acid, and the diamine liberated with alkali. It crystallised from alcohol in canary-yellow needles, m. p. 102—104° (Found: N = 11·5; S = 26·8. $C_{12}H_{10}N_2S_2$ requires N = 11·3; S = 26·01 per cent.).

The diamine was diazotised and the product coupled with the naphthols. The α-naphthol compound is scarlet, melts at 104°, and gives a deep violet colour with sulphuric acid.

Dimethoxythianthren.

Five c.c. of anisole were condensed with 4 c.c. of sulphur chloride. The reaction was completed on the water-bath after the evolution of hydrogen chloride had moderated. A viscous, heavy, red oil (*A*) was obtained on decomposition of the product with ice. This was shaken with sodium hydroxide solution to extract any phenolic compound, the unchanged anisole removed by distillation with steam, the residue dissolved in benzene, and the free sulphur removed with copper powder. The benzene solution deposited an oily substance which gave a beautiful green coloration with sulphuric acid.

The oil (*A*) was distilled at slightly diminished pressure, and an oil passed over at 175—185°. This oil is a mercaptan, because it gives a compound with mercuric chloride, dissolves in sodium hydroxide solution, and is oxidised by iodine. The distillate was oxidised with chromic acid mixture, or, better, with potassium permanganate to sulphonic acids, the sodium salts of which were isolated in the usual way. They were converted into the amides through the chlorides. The amides were crystallised from hot water, in which one, m. p. 116°, was sparingly soluble. The aqueous filtrate was evaporated to dryness; the residue, after crystallisation from alcohol, melted at 126—128°. Gatterman (*Ber.*, 1899, **32**, 1154) gives the m. p. of *m*-methoxybenzenesulphonamide as 128° and that of the *para*-compound as 116°. Therefore the foregoing oil is a mixture of *m*-methoxyphenyl mercaptan and *p*-methoxyphenyl mercaptan.

Condensation with Phenetole.

Phenetole was similarly condensed with sulphur chloride. A viscous, red oil, as in the case of anisole, was obtained, which yielded mercaptans on distillation; the mixture, however, has not yet been identified.

Diacetylthianthren.

Five c.c. of acetophenone mixed with 5 c.c. of sulphur chloride were diluted with 10 c.c. of carbon disulphide and the couple was quickly added. The liquid became deep red and a vigorous reaction ensued. After the violence of the reaction had abated, the mixture was warmed for an hour and then boiled for fifteen minutes on the water-bath. The product was decomposed with ice and the viscous mass obtained was freed from sulphur and repeatedly crystallised from a mixture of chloroform and alcohol. Diacetylthianthren melts at 88—91°, forms a phenylhydrazone (which melts with decomposition), develops a red coloration with sulphuric acid, and yields benzoic acid on oxidation with nitric acid (Found : S = 21·6. $C_{16}H_{12}O_2S_2$ requires S = 21·3 per cent.).

Dibenzylthianthren.

Diphenylmethane (2·2 grams) was condensed with 1·2 c.c. of sulphur chloride, carbon disulphide being slowly added during the reaction. The product, after decomposition with water, was freed from carbon disulphide and sulphur and crystallised from boiling diluted alcohol, when it melted at 196°, and gave a beautiful greenish-red fluorescence with sulphuric acid, which was destroyed by the addition of a trace of potassium nitrate (Found : C = 78·5;

H = 5·5; S = 16·25. $C_{26}H_{20}S_2$ requires C = 78·7; H = 5·05; S = 16·16 per cent.). Thioxanthen melts at 128° and gives no fluorescence with sulphuric acid (Graebe, *Annalen*, 1891, **263**, 14).

Condensation with Iodobenzene: Formation of Thianthren.

Iodobenzene (5 grams), dissolved in 10 c.c. of carbon disulphide, was slowly treated with 2 c.c. of sulphur chloride. Instantaneous separation of iodine took place. The reaction was completed by warming on the water-bath, and the product was poured into an ice-cold solution of sodium hydroxide. The precipitated resinous mass was freed from the last traces of iodine by sodium hydrogen sulphite and the white residue was extracted with boiling acetone. The acetone solution, after being concentrated, deposited crude thianthren, which was crystallised from alcohol. It then melted at 160° (mixed m. p. with thianthren, 160°), and gave the violet coloration with sulphuric acid characteristic of thianthren. During the first stage of the reaction, chlorine was evolved together with hydrogen chloride, but the evolution ceased during the progress of the reaction.

Iodobenzene and aluminium amalgam were warmed on the water-bath and refluxed with carbon disulphide for many hours without any change occurring. Sulphur chloride and iodobenzene were similarly heated on the water-bath without reacting. When, however, the amalgam was dropped into a mixture of sulphur chloride and iodobenzene, a vigorous reaction immediately began, with the instantaneous separation of iodine. The amount of iodine liberated roughly corresponded with that present in the iodobenzene.

Thianthrendicarboxylic Acid.

Three c.c. of freshly-distilled sulphur chloride were condensed with 2 c.c. of freshly-distilled benzoyl chloride by heating at 110° for two hours. The traces of unchanged constituents were removed by heating in a current of dry air, and the product was decomposed with ice and extracted with a dilute solution of sodium hydroxide, from which it was precipitated by dilute hydrochloric acid. The precipitate was crystallised from boiling water to which a little alcohol had been added. Pale yellow leaflets appeared while the liquid was still hot. The solution was filtered without cooling. The thianthrendicarboxylic acid crystallised in flakes, m. p. 204° (Found: S = 21·2. $C_{14}H_8O_4S_2$ requires S = 21·05 per cent. Found: in the barium salt, Ba = 31·1. $C_{14}H_6O_4S_2Ba$ requires Ba = 31·2 per cent.), gave a pink coloration with sulphuric acid, and lost carbon dioxide when it was melted and kept at 210° for some time; the cold mass crystallised from a mixture of chloroform and alcohol and was identified as thianthren.

Attempts to condense sulphur chloride with *p*-benzoquinone, ethyl benzoate, or nitrobenzene in the presence of aluminium amalgam were unsuccessful. In the case of *p*-iodotoluene, the iodine was entirely eliminated, but the product was resinous and resisted all attempts to crystallise it.

My best thanks are offered to Sir P. C. Rây, Dr. P. C. Mitter, and Dr. H. K. Sen for the interest they have taken in the work.

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CCXXIV.—*The Solubility of Glucinum Sulphate in Water and Sulphuric Acid at 25°.*

By HUBERT THOMAS STANLEY BRITTON.

THE solubility of glucinum sulphate in water and in sulphuric acid of varying concentrations was investigated at 25° by Wirth (*Zeitsch. anorg. Chem.*, 1913, **79**, 307). His investigations were carried out by allowing glucinum sulphate hexahydrate to attain equilibrium at 25° with the liquid phase. In this way, he found 1·96 grams of glucina in 100 grams of aqueous solution, but when the estimation was carried out by first raising the temperature of the mixture and then allowing it to attain equilibrium at 25°, 1·984 grams of glucina were found. From Wirth's data, it appears that the stable solid phase in equilibrium with aqueous solutions and with solutions in sulphuric acid of concentrations up to thirteen normal is the hexahydrate; above such concentration the tetrahydrate becomes the stable solid phase. This is contrary to the author's experience, for whenever crystals of glucinum sulphate have been prepared, either from aqueous or sulphuric acid solutions of varying concentration, they have invariably been the tetrahydrate. If, however, care is not taken to reduce the amount of ammonia adsorbed by the glucinum hydroxide before dissolving in sulphuric acid, crystals of glucinum ammonium sulphate will result (*vide* this vol., p. 1465).

Moreover, Wirth found that the solubility of glucinum sulphate in equilibrium with the hexahydrate was only 8·212 grams of glucinum sulphate in 100 grams of solution, whereas the author found that 100 grams of solution saturated with respect to the tetrahydrate contained 29·94 grams of glucinum sulphate. Incidentally, this figure appears to be in agreement with that found by Levi Malvano * at 30° (*Zeitsch. anorg. Chem.*, 1905, **48**, 452), namely, 30·5 grams. Hence, it was believed that at the ordinary temperature the stable solid phase was the tetrahydrate, and consequently if a metastable hydrate exists at such temperature, the amount of glucinum sulphate in solution in equilibrium with it, must be greater, and not less as found by Wirth.

Marignac (*Ann. chim. phys.*, 1873, [iv], **30**, 45) thought that he once obtained the hexahydrate by evaporating a supersaturated solution of sodium sulphate and glucinum sulphate, which, on exposure to air, effloresced. Levi Malvano (*loc. cit.*) obtained the hexahydrate from a commercial source. He states that he was only able to prepare the hexahydrate after many fruitless attempts, but that having once been prepared, the hexahydrate always crystallised from its aqueous solutions over a considerable range of temperature. Many methods, generally employed for the preparation of metastable hydrates, were adopted in trying to obtain the hexahydrate from solutions of the tetrahydrate, such as evaporation over sulphuric acid, subjection to cold and inoculation with crystals of the hexahydrate. In every case the tetrahydrate crystallised out. The successful method was to prepare a highly supersaturated solution by dissolving excess of either glucinum hydroxide or carbonate in concentrated sulphuric acid which had been slightly diluted, and then suddenly shaking at the ordinary temperature, when crystals containing six molecules of water separated out and were identical with the commercial product. They were quite stable in air. It is interesting to note Levi Malvano's observation that glucinum sulphate hexahydrate always crystallised from solutions made from it. He appears to have been under the impression that the nature of the solution varied with the hydration of the crystals from which the solution was made. This he further demonstrated by stating that the glucinum oxide obtained by precipitation with ammonium sulphide from solutions of the tetrahydrate was, on ignition, white, whereas that from hexahydrate solutions was blue. If the ignition of any glucinum hydroxide precipitate together with the filter-paper has not been sufficiently prolonged, the resulting ash is often faintly blue, no doubt due to the presence of a little carbon, for on further ignition the oxide becomes white. Parsons and Fuller (*Science*, 1906, **24**, 202) made repeated attempts to obtain the hexahydrate, but every attempt was futile, although they state that they faithfully followed Levi Malvano's instructions, besides trying other methods. Furthermore, Parsons ("Chemistry of Beryllium," 1908, p. 33) states that he obtained a bottle labelled "hexahydrate" from the dealers from whom Levi Malvano procured his supply; analysis of the contents proved them to be nothing but the regular tetrahydrate. Taboury (*Compt. rend.*, 1914, **159**, 180) was unable to prepare the hexahydrate. The author has also been unable to prepare the hexahydrate either according to Levi Malvano, or, as the following solubility determinations show, to Wirth.

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* Levi Malvano's analysis of glucinum sulphate tetrahydrate.
The data given for " SO_3 " are too high, being in reality those for " SO_4," and as the figures given for GlO are accurate, those for H_2O are correspondingly low.

EXPERIMENTAL.

Solutions of sulphuric acid of various normalities were warmed and saturated with pure glucinum sulphate tetrahydrate. They were then placed in a thermostat which had been carefully regulated at 25·0 ± 0·1°, and mechanically stirred until equilibrium between the liquid phase and the solid phase which had crystallised out had been attained. In all cases a day's stirring was found to be sufficient; examination of the liquid phase after further periods of stirring, from one to three days, showed no further change in its composition. After the solid phase had been allowed to settle completely, exactly 20 c.c. of the clear liquid phase were pipetted into a tared beaker and weighed. These solutions were made up to 250 c.c., and aliquot portions taken for the estimation of glucinum oxide and total sulphate. From these data, the amount of glucina in 100 grams of solution and also the final concentration of the free sulphuric acid were calculated.

To ascertain the nature of the solid phases, the following procedure was adopted. They were dried as well as possible between filter-papers, and the percentage of glucina estimated by strongly heating weighed quantities to constant weight (*vide* this vol., p. 1465).

Besides allowing the solid phases to crystallise out from supersaturated solutions at 25° as in the above determinations, further determinations were made by mixing solutions of sulphuric acid with excess of glucinum sulphate tetrahydrate crystals at room temperature and again stirring until both phases were in equilibrium one with the other. Again a day's stirring was all that was found necessary.

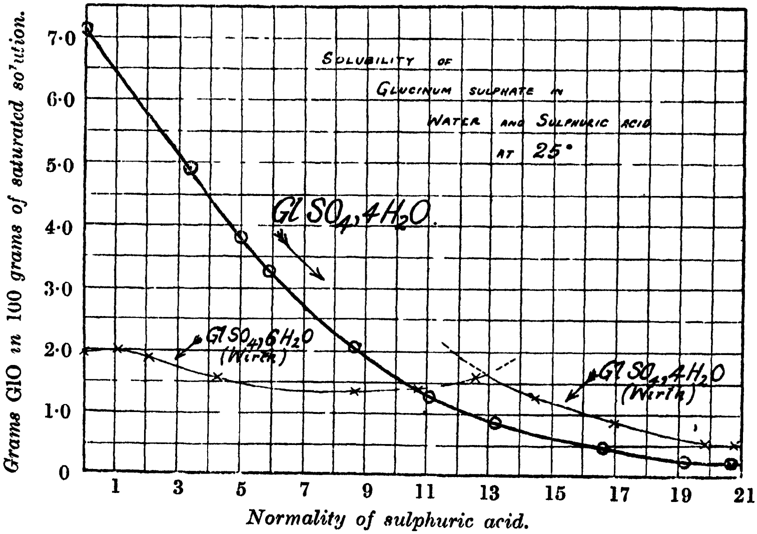
Results.

No.	Sulphuric acid. Normality.	Sulphuric acid. Percentage.	100 Grams of saturated solution contain grams of GlO.	100 Grams of saturated solution contain grams of $GlSO_4$.	Percentage of GlO in moist solid phase.*	Solid phase.*
1	Water	—	7·152	29·94	14·2	$GlSO_4,4H_2O$
2	3·39	12·91	4·900	20·51	13·5	"
3	5·01	19·17	3·800	15·91	13·7	"
4	5·87	22·36	3·261	13·65	13·5	"
5	8·66	32·04	2·057	8·61	14·0	"
6	11·10	40·34	1·254	5·25	13·1	"
7	13·23	46·59	0·846	3·54	13·2	"
8	16·70	55·50	0·486	2·04	13·5	"
9	19·23	62·02	0·234	0·98	13·4	"
10	20·65	66·07	0·213	0·89	13·2	"
11	20·70	66·10	0·206	0·86	13·4	"

* Compare percentage of GlO in $GlSO_4,2H_2O$ — 17·79; $GlSO_4,4H_2O$ — 14·17; $GlSO_4,6H_2O$ — 11·78.

All the above results, except Nos. 4, 10, and 11, were obtained from solutions which had been saturated with glucinum sulphate at a temperature above 25°, from which it was in each case found that glucinum sulphate tetrahydrate had crystallised. Nos. 4, 10, and 11 are the results obtained by allowing the solid phase—glucinum sulphate tetrahydrate—to attain equilibrium with solutions of sulphuric acid at 25°. These data are shown graphically in Fig. 1, using as ordinate and abscissa the same magnitudes as

FIG. 1.



were employed by Wirth. The curve obtained by Wirth is shown by the thinner lines.

Summary.

It will be seen that the curve is quite different from that obtained by Wirth. No evidence of the crystallisation of the hexahydrate from the more dilute solutions of sulphuric acid as found by Wirth has been obtained, no matter in which way the solubility determinations were carried out, and even that part of Wirth's curve which shows the composition of liquid phases in equilibrium with the tetrahydrate is somewhat higher than that represented above. From the smooth character of the curve representing solutions of glucinum sulphate in equilibrium with glucinum sulphate tetrahydrate, and from the fact that the tetrahydrate is the solid phase which is always deposited from saturated solutions under ordinary conditions, there appears to be no doubt that it is the stable hydrate. If a metastable hydrate exists, the amount of glucinum sulphate in solution in equilibrium with it being greater, the curve showing the concentrations of the solutions in equilibrium with it must lie above the curve given, which appears improbable. If the hexahydrate does exist, it appears that the conditions for its preparation have not yet been described.

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CCXXV.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part IV. Aryl Derivatives of Bisiminocamphor.*

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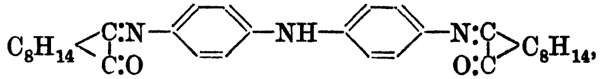
THE remarkably high molecular rotatory power displayed by products of condensing camphorquinone with aryldiamines was first noticed in connexion with *p*-phenylenebisiminocamphor (Forster and Thornley, T., 1909, **95**, 941). The rotation of this compound is greatly exceeded by that of 1 : 4-naphthylenebisiminocamphor (B. K. Singh and M. Singh, T., 1920, **117**, 1599), and we now find that the molecular rotatory power of *pp'*-bisiminocamphordiphenylamine, prepared from camphorquinone and *pp'*-diaminodiphenylamine, is even greater, as indicated below :

$[M]_D$.

	Chloroform.	Methyl alcohol.	Ethyl alcohol.	Pyridine.
pp'-Bisiminocamphordiphenylamine	11385°	12375°	14231°	13288°
1 : 4-Naphthylenebisiminocamphor	8175	9052	12071	13416
p-Phenylenebisiminocamphor	6088	5009	5289	6173

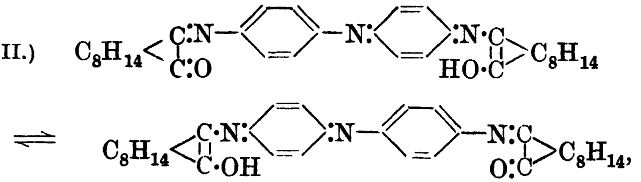
The conventional formula for *pp'*-bisiminocamphordiphenylamine, in which the continuity of conjugated linkings is broken, suggests

(I.)



an exception to the generalisation which has arisen from the study of such substances, namely, exaltation of rotatory power following concentration of conjugated linkings, azethenoid groups and benzene rings within a narrow molecular compass (Forster and Spinner, T., 1919, **115**, 889; B. K. Singh and M. Singh, *loc. cit.*). A similar anomaly is presented by camphorylaminophenyliminocamphor (Forster and Saville, this vol., p. 789), the molecular rotatory power of which exceeds that of *p*-phenylenebisiminocamphor. The case of *pp'*-bisiminocamphordiphenylamine, however, can be brought into harmony with the above generalisation by representing one of the benzene rings in the quinonoid form capable of displaying double symmetric tautomerism,

(II.)



the continuity of the conjugated linkings thus becoming restored. The fluorescence to be expected from such a compound is, in this case, weak, but a hydroxyl group is indicated by the greenish-red coloration with ferric chloride.

pp'-Bisiminocamphordiphenylamine is interesting also as a rare example of optically active dyes. Furthermore, it is phototropic and thermotropic, the yellow form changing to brown in sunlight; although the converse change does not occur in darkness, the brown modification rapidly becomes yellow above 75°. The remaining new compounds described in this paper, namely, oo'-*ditolylene*-

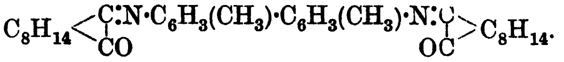
bisiminocamphor, oo′-*dimethoxydiphenylenebisiminocamphor*, and pp′-*diphenylenebisaminocamphor*, are in agreement with the above-mentioned generalisation; the first-named resembles *pp*′-diphenylenebisiminocamphor (Forster and Spinner, *loc. cit.*) in being dimorphous, but, unlike the authors quoted, we have reduced the latter substance to *pp*′-diphenylenebisaminocamphor. The effect of ortho-substitution on the rotatory power of *pp*′-diphenylenebisiminocamphor is very depressant, as indicated by the following measurements :

	$[M]_D$.	
	Chloroform.	Methyl alcohol.
pp′-Diphenylenebisiminocamphor :		
(*a*) Yellowish-green	5472°	——
(*b*) Golden-brown	5433	5020°
oo′-Ditolylenebisiminocamphor :		
(*a*) Green	3929	3274
(*b*) Golden-yellow	4007	3462
oc′-Dimethoxydiphenylenebisiminocamphor	2003	1576

Thus the sequence of substituents in order of diminishing rotatory power is $H > CH_3 > OCH_3$.

EXPERIMENTAL.

oo′-*Ditolylenebisiminocamphor*,



$$C_8H_{14}<\genfrac{}{}{0pt}{}{C{:}N\cdot C_6H_3(CH_3)\cdot C_6H_3(CH_3)\cdot N{:}C}{CO\qquad\qquad\qquad\qquad\qquad\qquad\qquad OC}>C_8H_{14}.$$

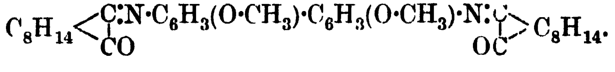
Camphorquinone (3·3 grams), tolidine dihydrochloride (2·85 grams), and excess of fused sodium acetate having been heated on the water-bath during four hours, the hard mass was extracted with 10 c.c. of cold alcohol, and the residue undissolved by water was crystallised fractionally from ether. The less soluble, preponderating component (*a*), which separated in long, green prisms, melts at 200—201°, and is readily soluble in chloroform, acetone, or hot ethyl alcohol, less so in methyl alcohol or ether; it is insoluble in cold ethyl alcohol or water (Found: N = 5·2. $C_{34}H_{40}O_2N_2$ requires N = 5·5 per cent.). The more soluble form (*b*), in golden-yellow prisms, melts at 198—199°, and is readily soluble in chloroform or acetone, less so in hot ethyl alcohol, and even more insoluble in hot methyl alcohol (Found : N = 5·2 per cent.). A mixture of *a* and *b* in equal amounts melts at 192—193°.

The following measurements of rotatory power, in common with all noted in this paper, are recorded as relating to the specified weight of material in 100 c.c. observed in a 2-dcm. tube, the initial reading having been taken within half-an-hour :

Solvent.	Gr./100 c.c.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·1280 (*a*)	29°	1·98°	773°	3929°
Methyl alcohol	0·1148 (*a*)	30	1·48	645	3274
Chloroform	0·0564 (*b*)	29	0·89	789	4007
Acetone	0·2708 (*b*)	21	3·98	736	3736
Methyl alcohol	0·0834 (*b*)	29	1·14	683	3470

The foregoing rotations remained unchanged during twenty-four hours.

oo′-*Dimethoxydiphenylenebisiminocamphor*,

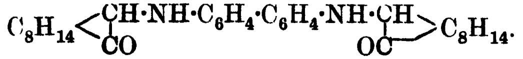


$$C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_3(O\cdot CH_3)\cdot C_6H_3(O\cdot CH_3)\cdot N{:}C\\ CO \qquad\qquad\qquad\qquad\qquad\qquad\qquad OC\end{array}>C_8H_{14}.$$

Camphorquinone (3·3 grams), dianisidine dihydrochloride (3·9 grams), and excess of sodium acetate having been heated on the water-bath during four hours, the residue undissolved by 10 c.c. of cold alcohol followed by water was crystallised from hot alcohol, which deposited thin, green prisms melting at 186° (Found: N = 4·84. $C_{34}H_{40}O_4N_2$ requires N = 5·18 per cent.). The substance dissolves very readily in chloroform or ether, less so in methyl alcohol and hot ethyl alcohol; it does not display mutarotation :

Solvent.	Gr./100 c.c.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·1670	22°	1·24°	371°	2003°
Methyl alcohol	0·2635	,,	1·53	290	1567

pp′-*Diphenylenebisaminocamphor*,



$$C_8H_{14}<\begin{array}{l}CH\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot CH\\ CO \qquad\qquad\qquad\qquad\qquad OC\end{array}>C_8H_{14}.$$

The *pp*′-diphenylenebisiminocamphor required in preparing the above product of reduction was divided into the less soluble component (*a*), which separated in yellowish-green prisms melting at 276°, and the more soluble component (*b*), forming golden-brown needles which melt at 274°, as described by Forster and Spinner (*loc. cit.*); a mixture of *a* and *b* in equal amounts melts at 267°. The substance does not display mutarotation :

Solvent.	Gr./100 c.c.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·2570 (*a*)	35°	5·86°	1140°	5472°
,, ...	0·4730 (*b*)	,,	10·71	1132	5433
Methyl alcohol ...	0·0908 (*b*)	29	1·90	1046	5020

pp′-*Diphenylenebisaminocamphor* was produced from both modifications on agitating ethereal solutions with zinc dust and 10 per cent. aqueous potassium hydroxide during six hours, the residue from evaporating the colourless solution being crystallised from hot alcohol, which deposited plates on cooling. The product from each source, and a mixture thereof, melted at 214° (Found: $C = 79{\cdot}4$; $H = 8{\cdot}28$. $C_{32}H_{40}O_2N_2$ requires $C = 79{\cdot}3$; $H = 8{\cdot}27$ per cent.). It is insoluble in water, but dissolves readily in chloroform or acetone; less so in methyl or ethyl alcohol.

Solvent.	Gr./100 c.c.	Temperature.	a_D.	$[a]_D$.	$[M]_D$.
Chloroform	0·2920	17°	0·57°	97·6°	472°
Methyl alcohol	0·0650	,,	0·10	76·9	372
Acetone	0·1435	,,	0·47	163·7	792

The substance, either solid or dissolved, becomes yellow in sunlight and remains in this form when left in darkness; the above solution in acetone, after six hours in sunlight, gave $[\alpha]_D$ 282°, whence $[M]_D$ 1365°, unchanged after twelve hours in darkness.

pp′-*Bisiminocamphordiphenylamine* (I or II).

Camphorquinone (1·66 grams), *pp′*-diaminodiphenylamine (1 gram), and fused sodium acetate were heated on the water-bath during two hours, the product being extracted with absolute alcohol, precipitated by water, and redissolved in hot alcohol, from which the substance crystallised (Found: $N = 8{\cdot}06$. $C_{32}H_{37}O_2N_3$ requires $N = 8{\cdot}48$ per cent.). It forms yellow prisms melting at 210—212°, and is insoluble in water, but dissolves in chloroform, benzene, or methyl alcohol, and less readily in ethyl alcohol. The alcoholic solution develops a greenish-red coloration with ferric chloride, and a deep, but transient, cherry red with mineral acids, becoming yellow with alkalis and returning with acids. It dyes wool yellow with alum, and somewhat deeper with chrome in an alcoholic bath of 2 per cent. The fluorescence in organic solvents is a feeble green, and there is no mutarotation:

Solvent.	Gr./100 c.c.	Temperature.	a_D.	$[a]_D$.	$[M]_D$.
Chloroform	0·1300	23°	5·98°	2300°	11385°
,, (brown form)	0·0364	30	1·72	2370	11731
Methyl alcohol	0·0554	23	2·77	2500	12375
Acetone	0·0376	19	1·99	2646	13097
Ethyl alcohol	0·0440	,,	2·53	2875	14231
Pyridine	0·1084	30	5·82	2685	13288

Exposure to sunlight during a few minutes converts the substance into a brown modification which does not revert in darkness, but becomes yellow when heated above 75°. The two forms and their mixture melt at the same temperature and have the same rotatory power.

For comparison with aryl derivatives of bisiminocamphor the parent substance, azocamphanone, was examined in the polarimeter (compare Forster and Zimmerli, T., 1910, **97**, 2165) :

Solvent.	Gr./100 c.c.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·2605	30°	0·98°	188°	616°
Methyl alcohol	0·1660	,,	0·76	229	750

Hydrochlorides of Bases in Condensation.

Free tolidine and dianisidine do not undergo condensation with camphorquinone even at high temperatures (120—125°) and with prolonged heating alone, or with sodium sulphate or zinc chloride. Action proceeds readily with the hydrochlorides, however, and benzidine combines in either form (compare G. M. Robinson and R. Robinson, T., 1918, **113**, 644).

One of us (M. S.) desires to make acknowledgment to the Punjab University for the Macleod-Kapurthala Research Scholarship which has enabled him to collaborate.

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CCXXVI.—*The Reversibility of the Michael Reaction.*

By CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL.

ALTHOUGH the condensation of αβ-unsaturated esters with sodium derivatives of compounds of the type of ethyl malonate, generally known as the Michael reaction, is one of the most valuable methods of synthesis in the hands of the organic chemist, its mechanism and controlling conditions appear to have received singularly little attention. This is particularly remarkable when it is recalled that the mechanism of the acetoacetic ester condensation, of the Perkin reaction, and indeed of most of the important synthetical processes, has been the subject of protracted controversies.

During the course of an inquiry into the reason why certain attempts to produce derivatives of methanetriacetic acid by means of the Michael reaction met with no success, facts were discovered (Ingold and Perren, this vol., p. 1865) which strongly suggested that the Michael condensation is a reversible process, at least in the particular series of compounds dealt with. Therefore it seemed of interest to ascertain (*a*) whether the reversibility of the reaction is a general phenomenon, (*b*) further, supposing this to be so, how the tendency towards reversion is conditioned by the structures of the substances concerned, and (*c*), finally, how the equilibrium, in any particular case, may be displaced in a desired direction by adjusting the experimental conditions. The present paper is a preliminary attempt to find the answers to these questions, which will now be discussed in turn.

(*a*) It is convenient to adopt the equation

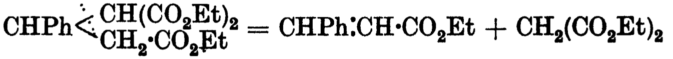
$$U + M = C \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where U is an unsaturated ester, M the sodio-derivative of malonic ester or some other ester of a similar type, and C the condensation product, as a symbolic expression in general terms of any Michael condensation; the converse equation

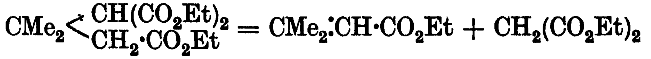
$$C = U + M \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

will therefore denote any retrograde Michael condensation. Now it so happens that in all the instances previously recorded (*loc. cit.*) reaction (ii), when observed at all, proceeded so nearly to completion that it was impossible to obtain the condensation product C by the corresponding direct reaction (i). C had to be produced by an indirect means (introducing the substituted acetic acid chains in a different order) which, however, cannot be employed excepting in the methanetriacetic acid series. Therefore, in order to establish the generality of the phenomenon, it was essential to select for examination instances (outside the methanetriacetic acid series) in which there would appear to be a more even balance between the reactions (i) and (ii). On examining the literature, and, in particular, the yields of condensation products obtained by various investigators, it quickly became apparent that the vast majority of the recorded instances of condensations between ethyl malonate and esters of the acrylic acid series probably belong to this category, and it was decided, consequently, to approach the problem by reinvestigating two typical condensations which have some claim to be regarded as being amongst the most classical instances of the Michael reaction. The examples chosen were (α) the condensation of ethyl cinnamate with ethyl malonate, the first recorded instance of the reaction (Michael, *J. pr. Chem.*, 1887, [ii], **35**, 351), and (β) the condensation of ethyl ββ-dimethylacrylate with ethyl malonate, a reaction which formed the starting-point of most of the earlier important synthetical experiments dealing with the constitution of camphor and its degradation products (Goodwin and Perkin, P., 1894, **10**, 64; T., 1896, **69**, 1472; Auwers, *Ber.*, 1895, **28**, 1130; *Annalen*, 1896, **292**, 145; Perkin and Thorpe, T., 1899, **75**, 51).

In the first place, it was necessary to show that the retrograde reaction could be realised in these instances. This presented no difficulty, for when the pure condensation products (ethyl β-phenylpropane-αα γ-tricarboxylate and ethyl ββ-dimethylpropane-ααγ-tricarboxylate) were dissolved in alcoholic solutions containing equivalent quantities of sodium ethoxide, and heated at 100° under the conditions usually employed in carrying out ordinary Michael reactions, fission occurred to the extent of approximately 60 per cent. in the sense of the following equations:



$$\mathrm{CHPh}{<}\begin{matrix}\mathrm{CH(CO_2Et)_2}\\ \mathrm{CH_2{\cdot}CO_2Et}\end{matrix} = \mathrm{CHPh{:}CH{\cdot}CO_2Et} + \mathrm{CH_2(CO_2Et)_2}$$



$$\mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH(CO_2Et)_2}\\ \mathrm{CH_2{\cdot}CO_2Et}\end{matrix} = \mathrm{CMe_2{:}CH{\cdot}CO_2Et} + \mathrm{CH_2(CO_2Et)_2}$$

From this result the attainment of equilibria appears to follow as a necessary corollary. Moreover, it rapidly became clear in the course of the experimental investigation that essentially *the same* equilibrium is invariably attained, no matter whether it be approached by the direct or by the retrograde process; no matter, therefore, whether the starting-point be the pure product *C*, or a mixture of equivalent amounts of the constituent esters *U* and *M*, or any mixture of this mixture with the ester *C*, always provided that sufficient time be allowed for the equilibrium to be reached.

(*b*) It would be a matter of the greatest interest to obtain a collection of accurate values for the equilibria with ethyl malonate at different temperatures and concentrations of a series of α- and β-substituted acrylic esters. Unfortunately, the method of separating by fractional distillation the three esters present at equilibrium is a cumbersome and inaccurate way of estimating their relative proportions, but for lack of suitable analytical processes this has been the method employed in the present investigation. However, where similar experimental conditions have been used, the yields obtained are in moderately close agreement with those recorded by previous workers (*loc. cit. Vide* also Michael, *Ber.*, 1900, **33**, 3748; Perkin, T., 1896, **69**, 1467), and the following table is probably a not very inaccurate statement of the equilibria which can be reached under the customary experimental conditions (Solvent: 99·8 per cent. ethyl alcohol. Concentration: 300 grams of alcohol for gram-molecular quantities of the reactants).

	Yield of *C* (per cent.).	
Condensation Product (*C*).	Temp. 100°.	Temp. 25°.
Ethyl β-methylpropane-ααγ-tricarboxylate	65	?
,, β-phenylpropane-ααγ-tricarboxylate	35	70
,, ββ-dimethylpropane-ααγ-tricarboxylate ...	30	50
,, αββ-trimethylpropane-ααγ-tricarboxylate ...	trace ?	?

The effect on ring closure of the *gem*-dimethyl group, and in general of substituents of considerable atomic or molecular volume, has been emphasised in two recent communications (Ingold, this vol., pp. 305, 951). It has been proved, for instance, that derivatives of ββ-dimethylglutaric acid pass, by the interaction of substituents attached to the two acetic acid chains, into cyclic compounds more readily than do similar derivatives of glutaric acid. There is much evidence tending to show that the acetic acid residues are in closer proximity in the former case than in the latter. It seems, therefore, very reasonable to suppose, for instance, that the acetic and malonic ester chains in ethyl ββ-dimethylpropane-ααγ-tricarboxylate are in closer proximity than those in ethyl β-methylpropane-ααγ-tricarboxylate; further, because the accumulation of bulky groups in a restricted space is invariably a condition of instability, it must follow that the convergence of these chains caused by the groups attached to the β-carbon atom of the glutaric acid derivative must determine its tendency towards decomposition into smaller molecules. It is obvious from the table that this tendency towards disruption is greater in the case of the ββ-dimethyl compound than with the β-methyl analogue. The single phenyl group occupies a position intermediate between the single methyl group and the *gem*-dimethyl group, whilst the remarkable effect of introducing a substituent into the acetic acid chain, an effect so noticeable in the methanetriacetic acid series (*loc. cit.*), is again observed in the case of the trimethyl compound.*

We have, therefore, a method of considerable potential value for determining the effect of substitution on the stability of a carbon chain, but it is unfortunate that in this field, in which certain thermal and thermochemical determinations would be of the greatest service, very few measurements have been made. It would appear, however, that the heat of a reaction of type (i) is usually positive, and that, as follows from the formula $d \log_e K/dT = - QR^{-1}T^{-2}$, the equilibrium moves in the direction which favours the product C when the temperature is reduced. Moreover, the same formula shows that Q must be greater for the condensation between ethyl malonate and ethyl cinnamate than for that between ethyl malonate and ethyl dimethylacrylate, although no direct experimental determinations have as yet been made. As Nernst (*Wied. Annalen*, 1894, **53**, 57), Bödlander (*Zeitsch. physikal. Chem.*, 1898, **27**, 55), and others have shown, *Q* and the osmotic work *A* do not differ by much if no gaseous substances take part in the equilibrium, and it is the common value towards which *Q* and *A* converge which is the true measure of the stability of the molecule.

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* The effect of the electrochemical character of substituent groups is also easily appreciable, as many instances, which lie without the scope of this paper, show. The larger yields of condensation products obtained when ethyl malonate is replaced by ethyl cyanoacetate (compare, for instance, Perkin and Thorpe, T., 1899, **75**, 52) may be attributed in part to the more intense polar character of the CN-group, but here again the difference is in the sense which accords with the relation between the molecular volumes of the groups concerned.

(*c*) The above considerations show that if it be desired to prepare the compound *C* by means of reaction (i), there are certain factors by adjusting which the equilibrium may be caused to move in the direction favouring the production of that substance. Thus the equilibrium may be disturbed by some further change, either physical or chemical. To take a single instance of the effect of concentration, if two-thirds of the theoretical quantity of ethyl cinnamate be used in the preparation of ethyl β-phenylpropane-ααγ-tricarboxylate, the yield obtained on allowing the reaction to take place at 25° (other conditions being as indicated on p. 1978) is more than 80 per cent. of the theoretical, calculated on the ethyl cinnamate employed.

The table on p. 1978 shows in a very clear manner the effect of lower temperatures on the equilibrium quantities of the condensation products. It is curious that none of the investigators previously referred to, for whom the preparation of ethyl ββ-dimethylpropane-ααγ-tricarboxylate was the starting-point of their synthetical experiments, appears to have tried the effect of lower temperatures with a view to improve the yields, which, under the conditions they employed, were always poor. Michael, on the other hand, was fully aware that better yields of ethyl β-phenylpropane-ααγ-tricarboxylate could be obtained by conducting the reaction in the cold, but he did not appreciate the fact that the cause of this lay in the simultaneous occurrence of the retrograde process.

EXPERIMENTAL.

The general plan of these experiments, as well as the results obtained, has been fully described above, and only a few minor details need be added here, since the method of conducting Michael condensations is well known.

Identity and Purity Criteria.

The ethyl malonate and ethyl cinnamate employed were carefully purified by distillation, and the ethyl β-phenylpropane-ααγ-tricarboxylate required for the experiments on the retrograde reaction was prepared from the other two esters by condensation at a low temperature. It was purified by distillation (b. p. 220—224°/

25 mm.), and its purity controlled by analysis (Found: C = 63·9; H = 7·3. Calc., C = 64·3; H = 7·1 per cent.).

The products of the retrograde reaction (type ii) were separated by fractional distillation. The ethyl cinnamate was identified by its boiling point (270—274°), by analysis (Found: C = 74·6; H = 6·9. Calc., C = 75·0; H = 6·8 per cent.), and by hydrolysis to cinnamic acid, and the ethyl malonate by its boiling point (195°) and by conversion into malonamide.

Ethyl dimethylacrylate was prepared from ethyl α-bromo*iso*valerate and quinoline (Perkin, *loc. cit.*) and was so distilled as to remove the trace of volatile impurity that often causes the freshly-distilled ester to turn pink. The ethyl ββ-dimethylpropane-ααγ-tricarboxylate, prepared from ethyl dimethylacrylate and ethyl malonate by condensation at 35°, was purified by distillation (b. p. 181°/28 mm.), and its purity checked by analysis (Found: C = 58·4; H = 8·4. Calc., C = 58·3; H = 8·3 per cent.).

The ethyl dimethylacrylate isolated from the retrograde reaction (type ii) was identified by its boiling point (155°), by analysis (Found: C = 65·3; H = 9·3. Calc., C = 65·6; H = 9·4 per cent.), and by hydrolysis to dimethylacrylic acid. The ethyl malonate was identified as in the previous instance.

Times Required to Attain Equilibria.

Equilibrium is attained more rapidly between ethyl malonate, ethyl cinnamate, and ethyl β-phenylpropane-ααγ-tricarboxylate than between ethyl malonate, ethyl ββ-dimethylacrylate, and ethyl ββ-dimethylpropane-ααγ-tricarboxylate. In the former case, heating for six hours at 100° or for one week at 25° suffices for the approximate attainment of the equilibria characteristic of these temperatures, whilst in the latter it is better to heat the mixture for about twenty-four hours at 100° or for two weeks at 35°.

Method of Conducting Retrograde Reactions (Type ii). Example: Decomposition of Ethyl β-Phenylpropane-ααγ-tricarboxylate into Ethyl Cinnamate and Ethyl Malonate.

The following instance illustrates the method employed. Ethyl β-phenylpropane-ααγ-tricarboxylate (100 grams) was added to a solution of sodium (6·8 grams) in absolute ethyl alcohol (89 grams), and the mixture heated at 110° in a closed vessel for seven hours. It was then cooled as quickly as possible, poured into dilute hydrochloric acid, and the esters isolated by extraction with ether in the usual manner. On distilling the product under diminished pressure, 30 grams (30 per cent.) of ethyl β-phenylpropane-ααγ-tricarboxylate were recovered (b. p. 220—224°/25 mm.), together with a more volatile fraction, which, on refractionating at the ordinary pressure, yielded 31 grams (60 per cent.) of ethyl cinnamate (b. p. 270—274°), and a quantity of ethyl malonate. Malonic acid also was recovered from the aqueous liquors. Ten per cent. of the material remained to be accounted for as experimental losses.

We gratefully acknowledge our indebtedness to Professor J. F. Thorpe for his interest in this investigation. Part of the cost was defrayed from a grant made by the Chemical Society, to whom also we wish to record our thanks.

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SOUTH KENSINGTON, S.W.7. [*Received, October 14th*, 1921.]

CCXXVII.—*Complex Metallic Ammines. Part VI.* cis-*Phthalato-,* cis-*Homophthalato-, and other Diethylenediaminecobaltic Salts.*

By JAMES COOPER DUFF.

IN Part V (this vol., p. 385), a number of cobaltammine salts were described, which were derived from six dibasic aliphatic acids and contained a seven-membered ring in the complex. Werner (*Annalen*, 1911, **386**, 26, 81) was of the opinion that complexes containing a higher number of atoms to the ring than six could not be obtained. In Part V it was pointed out that Werner was using acids of a type unsuitable to the formation of a ring of more than six atoms in the complex.

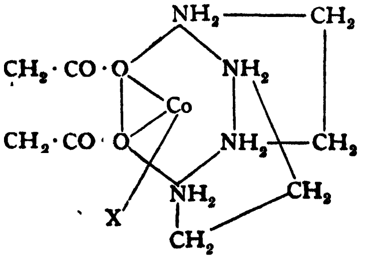
The results obtained in Part V (*loc. cit.*) showed that the complex could be enlarged in molecular size, and it was therefore of interest to investigate what increase in size of the complex was possible. Price and Brazier (T., 1915, **107**, 1367) showed that an eight-membered ring was possible by introducing the sulphur atom into the ring, using for the purpose sulphonyldiacetic acid. It was decided to investigate the results obtained by using aromatic dibasic acids. In addition to the ring formation, the complex would be increased in molecular size by the benzene ring.

Phthalic acid was found to give crystalline compounds containing the phthalato-radicle in the complex. This means that the complex in these compounds contains a seven-membered ring and the benzene ring in addition. Phthalato-compounds, as is to be expected, are formed more readily than the corresponding succinatocompounds (*loc. cit.*, p. 387), since phthalic acid gives an anhydride more readily than does succinic acid.

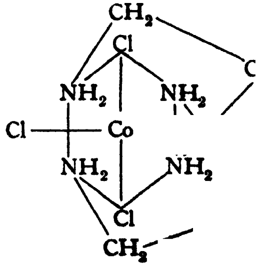
Price and Duff (T., 1920, **117**, 1072) have described the introduction of the sulphoacetato-radicle into the complex. It has now been found possible to introduce the benzylsulphoacetato-radicle. *o*-Sulphobenzoic and bromobenzene-3 : 4-disulphonic acids have been used and both yield crystalline compounds which contain a seven-membered ring, and a benzene ring in addition. These results correspond with those obtained from sulphoacetic acid and methionic acid (Price and Duff, *loc. cit.*), but lead to one more carbon atom in the ring system.

Glutaric acid has been tried for the purpose of forming an eight-membered ring in the complex, but it has not produced any crystallisable compounds. Homophthalic acid has, however, given crystallisable compounds which represent the first compounds with a complex containing eight atoms in the ring, without the presence of sulphur.

The compounds which have been obtained show that it is possible to increase the size of the complex considerably more than Werner considered possible. The results give support to the shell formula suggested by Friend (this vol., p. 1045), since the zone round the cobalt atom is not increased in size by these acids, as is the case with the co-ordination formula suggested by Werner. It should be noted that the formula, which Friend (*loc. cit.*) gives for succinato-diethylenediaminecobaltic salts, is not the most probable. Werner has shown that the corresponding carbonato- and oxalato- salts can be resolved into optically active isomerides. In the shell formula, cobalt cannot be considered asymmetric, and the optical activity is due to nitrogen being a member of two ring systems. This is shown by having the ethylenediamine molecules interlocking. This interlocking is rendered more probable by the more stable character of the compounds compared with those formed from ammonia. Formula I would then represent the succinato-salts.



(I.)

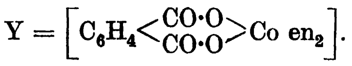


(II.)

The author is not prepared to support the conclusion of Friend (*loc. cit.*) that oxygen atoms from an acid like succinic or fumaric acid could take up *para*-positions in the shell formula. *Trans-* or *para-* salts of the tetrammine series change colour in solution from green to purple, and Werner has shown conclusively that they are then *cis-* or *ortho-* salts, and can only be reconverted to *trans-* or *para-* salts by excess of a strong mineral acid like hydrochloric or hydrobromic acid. The formula of *trans*-dichlorodiethylenediaminecobaltic chloride, expressed by the shell theory, would be best written as formula II, so that in both the *cis-* and *trans-* salts the ethylenediamine molecules are interlocking. The shell theory, as Friend (*loc. cit.*) points out, receives even stronger support from compounds like the carbonato-pentammine salts.

EXPERIMENTAL.

cis-*Phthalatodiethylenediaminecobaltic Salts*, YX, where



$$Y = \left[C_6H_4{<}\begin{matrix}CO{\cdot}O\\CO{\cdot}O\end{matrix}{>}Co\ en_2\right].$$

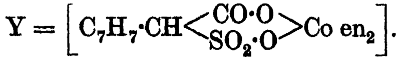
The *bromide*, YBr,$3H_2O$, separated in minute, purplish-red plates when a hot solution of 2·60 grams of phthalic acid was poured into a boiling solution of 5 grams of carbonatodiethylenediaminecobaltic bromide in 100 c.c. of water, and the mixed solution was concentrated to a small bulk on the water-bath, and left in the ice chest (Found: Co = 12·21; Br = 16·52; H_2O = 11·52. $C_{12}H_{20}O_4N_4BrCo,3H_2O$ requires Co = 12·36; Br = 16·76; H_2O = 11·32 per cent.).

The phthalato-radicle was entirely in the complex, since no reaction could detect its presence until the bromide was well boiled with dilute hydrochloric acid, when phthalic acid could be crystallised out on cooling.

The *nitrate*, $YNO_3,2\frac{1}{2}H_2O$, was obtained in fine, short, mauve needles by precipitating a solution of 3 grams of the bromide with 1·20 grams of silver nitrate, filtering and evaporating to small bulk (Found: Co = 12·99; N = 15·35; H_2O = 9·91. $C_{12}H_{20}O_7N_5Co,2\frac{1}{2}H_2O$ requires Co = 12·99; N = 15·43; H_2O = 9·91 per cent.).

The *hydrogen phthalate*, $Y{\cdot}CO_2{\cdot}C_6H_4{\cdot}CO_2H$, was obtained in microscopic, pink plates by adding 5·2 grams of phthalic acid to a boiling solution of the carbonato-base, prepared from 5 grams of the carbonato-bromide in 100 c.c. of water and 4 grams of freshly-prepared, moist silver oxide. The resulting solution was evaporated on the water-bath, and the salt separated in increasing quantity as the evaporation proceeded. It is almost insoluble in cold water (Found: Co = 11·38; N = 11·01. $C_{20}H_{25}O_8N_4Co$ requires Co = 11·61; N = 11·03 per cent.).

cis-*Benzylsulphoacetatodiethylenediaminecobaltic Salts*, YX, where



$$Y = \left[C_7H_7\cdot CH<\begin{matrix}CO\cdot O\\SO_2\cdot O\end{matrix}>Co\ en_2\right].$$

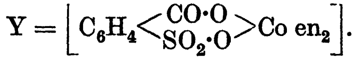
The *bromide*, $YBr,2H_2O$, was obtained in minute, red, flattened needles by adding 3·61 grams of benzylsulphoacetic acid in 50 c.c. of water to a hot solution of 5 grams of the carbonato-bromide in 100 c.c. of water, and then concentrating to low bulk and keeping for four weeks in the ice chest (Found: Co = 11·38; Br = 15·32; H_2O = 6·88. $C_{13}H_{24}O_5N_4BrSCo,2H_2O$ requires Co = 11·23; Br = 15·28; H_2O = 6·88 per cent.).

The *normal benzylsulphoacetate*, $Y\cdot CO_2\cdot C_8H_8\cdot SO_3\cdot Y,4H_2O$, was obtained in the attempt to prepare the acid salt from two molecular proportions of the acid and one of the carbonato-base. After evaporation to low bulk and keeping for several weeks in the ice chest, the normal salt separated in microscopic, pink crystals (Found: Co = 10·58; N = 9·95; H_2O = 6·48.

$C_{35}H_{56}O_{15}N_8S_3Co_2,4H_2O$

requires Co = 10·58; N = 10·05; H_2O = 6·46 per cent.).

cis-o-*Sulphobenzoatodiethylenediaminecobaltic Salts*, YX, where



$$Y = \left[C_6H_4<\begin{matrix}CO\cdot O\\SO_2\cdot O\end{matrix}>Co\ en_2\right].$$

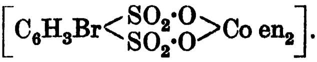
The *bromide*, YBr,H_2O, was obtained in microscopic, purple-red crystals after the gradual addition of a solution of 3·27 grams of sulphobenzoic acid to a boiling solution of 5 grams of the carbonato-bromide in 100 c.c. of water, and evaporation to low bulk. Gradual addition of the acid was necessary to avoid the formation of the hydrogen sulphobenzoate, which was otherwise found to separate (Found: Co = 12·18; Br = 16·58; H_2O = 3·89.

$C_{11}H_{20}O_5N_4BrSCo,H_2O$

requires Co = 12·36; Br = 16·76; H_2O = 3·77 per cent.).

The *hydrogen sulphobenzoate*, $Y\cdot SO_3\cdot C_6H_4\cdot CO_2H$, was obtained in minute, pink plates from two molecular proportions of the acid and one of the carbonato-base in the usual way. It is much more soluble in water than the corresponding phthalato-hydrogen phthalate (Found: Co = 9·99; N = 9·55. $C_{18}H_{25}O_{10}N_4S_2Co$ requires Co = 10·16; N = 9·66 per cent.).

cis-*Bromobenzene*-3 : 4-*disulphonatodiethylenediaminecobaltic Salts*, YX, where Y =

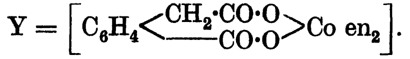


$$\left[C_6H_3Br{<}\begin{matrix}SO_2{\cdot}O\\SO_2{\cdot}O\end{matrix}{>}Co\ en_2\right].$$

Bromobenzene-3 : 4-disulphonic acid was selected because it contains the two sulphonic acid groups in the *ortho*-position, and it was found to behave in a different manner from that of any of the other acids used (compare in this respect the results obtained with methionic acid, which is also a disulphonic acid; T., 1920, **117**, 1073). With the carbonato-bromide the acid produces the normal bromobenzene-3 : 4-disulphonate described below and hydrogen bromide is set free; the latter reacts with some of the carbonato-bromide to give the green *trans*-salt, ($Br_2Co\ en_2$)Br, which could be detected in crystalline form in the evaporated solution.

The *bromobenzene*-3 : 4-*disulphonate*, $Y{\cdot}SO_3{\cdot}C_6H_3Br{\cdot}SO_3{\cdot}Y$, was obtained in the usual way from three molecular proportions of the acid and two of the carbonato-base. When the two solutions were mixed, separation of the salt began almost at once, and more was obtained by evaporation at the room temperature in a vacuum desiccator over sulphuric acid. It was found that evaporating by heating caused the solution to turn brown, apparently through decomposition. The normal salt was obtained in pale pink, microscopic crystals (Found: Co = 8·93; N = 8·59; S = 14·56. $C_{26}H_{41}O_{18}N_8Br_3S_6Co_2$ requires Co = 9·05; N = 8·60; S = 14·74 per cent.).

cis-*Homophthalatodiethylenediaminecobaltic Salts*, YX, where



$$Y = \left[C_6H_4{<}\begin{matrix}CH_2{\cdot}CO{\cdot}O\\CO{\cdot}O\end{matrix}{>}Co\ en_2\right].$$

The *bromide*, YBr, was not obtained in a crystalline form, although a red powder answering to it in analysis and properties was obtained when ethyl alcohol was added to the very concentrated syrup obtained after evaporating a solution of 5 grams of the carbonato-bromide, to which 2·82 grams of homophthalic acid had been added. The powder obtained takes up moisture from the air unless it has been repeatedly washed with acetone and, finally, with ether. Although insoluble in ethyl alcohol, the powder is readily soluble in methyl alcohol.

The *thiocyanate*, $Y{\cdot}SCN,H_2O$, was obtained from the foregoing product by adding 2 grams of ammonium thiocyanate to a strong solution of 2 grams of the bromide. The thiocyanate separates at first in a viscid condition, but after being well washed with water and redissolved in warm water, it can be crystallised in minute, purple,

irregular plates, after evaporation in a desiccator (Found: Co = 13·50; N = 15·93; H_2O = 4·28. $C_{14}H_{22}O_4N_5SCo,H_2O$ requires Co = 13·61; N = 16·18; H_2O = 4·16 per cent.).

The *hydrogen homophthalate*, $Y{\cdot}CO_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$, was obtained in pink, microscopic needles from two molecular proportions of the acid and one of the carbonato-base in the usual way, although addition of a few drops of alcohol after evaporation, and keeping for four weeks in the ice-chest were required to cause crystallisation. The salt was obtained in good yield. It is much more soluble in cold water than the corresponding product obtained from phthalic acid (Found: Co = 10·85; N = 10·51. $C_{22}H_{29}O_8N_4Co$ requires Co = 11·00; N = 10·45 per cent.).

trans-*Dichlorodiethylenediaminecobaltic Salts.*

Price and Brazier (T., 1915, **107**, 1713) have described a series of additive compounds formed from certain dibasic aliphatic acids and their acid salts of *trans*-dichlorodiethylenediaminecobalt. The five acids employed in the preparation of the *cis*-compounds described above have been used to discover their behaviour with *trans*-dichlorodiethylenediaminecobaltic chloride.

Benzylsulphoacetic acid, unlike malonic acid, does not give an additive compound. It agrees in its behaviour with sulphoacetic acid (T., 1920, **117**, 1075).

trans-*Dichlorodiethylenediaminecobaltic hydrogen benzylsulphoacetate*, $(Cl_2Co\ en_2)SO_3{\cdot}C_8H_8{\cdot}CO_2H$, separated readily in grass-green needles when 2 grams of *trans*-dichlorodiethylenediaminecobaltic chloride were stirred into a solution of 2 grams of benzylsulphoacetic acid in 30 c.c. of water (Found: Co = 12·25; Cl = 14·55. $C_{13}H_{25}O_5N_4Cl_2SCo$ requires Co = 12·31; Cl = 14·81 per cent.).

Phthalic acid, like succinic acid, does not form an additive compound. As phthalic acid is not sufficiently soluble in water, it was necessary to use sodium hydrogen phthalate. An alcoholic solution was tried unsuccessfully.

trans-*Dichlorodiethylenediaminecobaltic hydrogen phthalate* separated almost quantitatively in emerald-green plates when a solution of 5 grams of sodium hydrogen phthalate in 25 c.c. of water at 50° was poured into a cold solution of 4 grams of the *trans*-dichloro-chloride in 20 c.c. of water (Found: Co = 14·09; Cl = 16·81. $C_{12}H_{21}O_4N_4Cl_2Co$ requires Co = 14·21; Cl = 16·63 per cent.).

Sulphobenzoic acid also does not give an additive compound.

trans-*Dichlorodiethylenediaminecobaltic hydrogen sulphobenzoate*, $(Cl_2Co\ en_2)SO_3{\cdot}C_6H_4{\cdot}CO_2H$, separated in dark green, elongated plates on adding 2 grams of the *trans*-dichloro-chloride to a solution of 4 grams of sulphobenzoic acid in 25 c.c. of water and keeping for two hours (Found: Co = 13·00; Cl = 15·61. $C_{11}H_{21}O_5N_4Cl_2SCo$ requires Co = 13·08; Cl = 15·72 per cent.).

Homophthalic acid was tried, both as the free acid and as the acid sodium salt, with the *trans*-dichloro-chloride, but no crystals could be obtained either of an additive compound or of an acid homophthalate.

Bromobenzene-3 : 4-disulphonic acid behaves differently from all acids previously used, in its action on the *trans*-dichloro-chloride. When solutions of the two substances were mixed, instead of a green *trans*-dichloro-salt forming, all the chlorine was displaced by the organic acid and a *cis*-salt soon separated in microscopic, pink crystals. This was found to be the bromobenzene-3 : 4-disulphonatodiethylenediaminecobaltic bromobenzene-3 : 4-disulphonate already described (Found: Co = 9·10; N = 8·65. Calc., Co = 9·05; N = 8·60 per cent.).

Since the work of Price and Brazier (*loc. cit.*), no other acids have so far yielded additive compounds of the type they describe.

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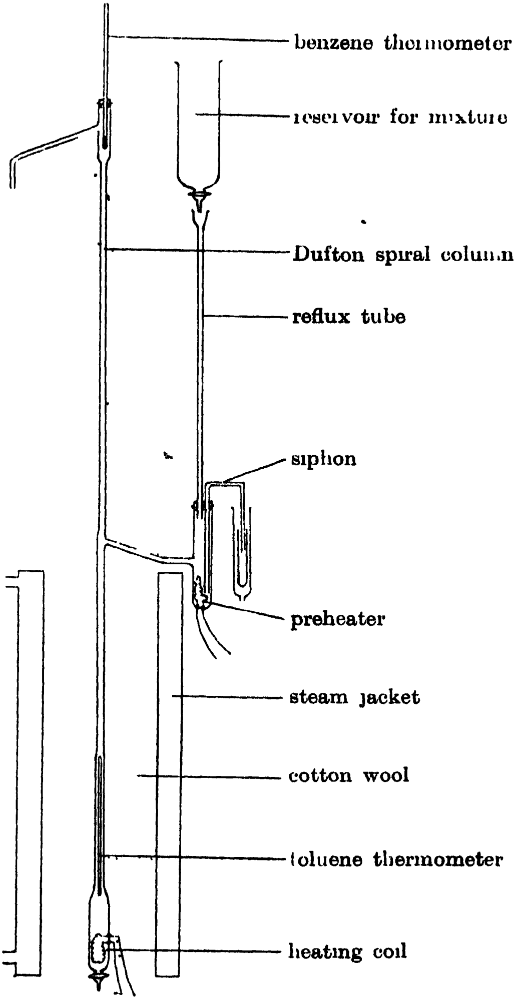
CCXXVIII.—*The Separation of Miscible Liquids by Distillation.*

By Arthur Felix Dufton.

The object of the present research is the investigation in the laboratory of continuous distillation. This involves the construction of continuous stills capable of effecting in the laboratory the perfect separation of a simple binary mixture such as benzene and toluene, which has hitherto not been achieved, and the study of their behaviour. A quantity, termed the thermal efficiency, has been defined by the author (*Phil. Mag.*, 1921, [vi], **42**, 633) to afford a comparison of the performance of stills and a measure of the approach towards theoretical perfection.

A typical column for continuous distillation consists of a vertical tube into the middle of which the mixture to be distilled is introduced. The more volatile component is collected at the top of the column and the less volatile at the bottom. The upper part, that is, the portion above the point at which the mixture is introduced, behaves exactly like a still-head for discontinuous working and must lose a certain amount of heat either throughout its length or to a condenser at the top. To the lower part of the column, on the other hand, heat must be supplied either throughout the length or to a boiler at the bottom. When the whole of the heat is supplied at the bottom, loss of heat from the column must be reduced to a minimum.

FIG. 1.



As the only form of still-head capable of giving perfect separation in the laboratory appeared to be the column devised by Dr. S. F. Dufton (*J. Soc. Chem. Ind.*, 1919, **38**, 45T) for the separation of small quantities of liquids, it was decided to construct a continuous model upon the same principle. This type of column is made by creating a spiral track in a narrow annulus between a glass tube and an inner core upon which a spiral of wire is wound. Descending liquid seals the wire to the walls of the annulus and causes the ascending vapour to pass along the spiral track.

The first successful column made was 200 cm. long and the internal diameter increased from 0·45 cm. at the top to 0·9 cm. at the bottom (Fig. 1). Heat was supplied electrically at the bottom of the still by means of a wire coil immersed in the toluene and the rate of heating was measured by means of a watt-meter. To obviate any loss of heat from the lower half of the column, a thick lagging of cotton-wool was employed and this lagging was surrounded by a steam-jacket. As the temperature at the bottom of the still was 110° and at the middle of the still 90°, this protection was practically ideal. The upper half of the column was also lagged with cotton-wool.

The mixture to be separated was fed down a short reflux-tube into a small flask, where it was electrically preheated to its boiling point, and delivered into the middle of the column. A siphon maintained the level in the preheater constant and ensured a constant feed-pressure. The rate of feeding was regulated by altering the siphon level.

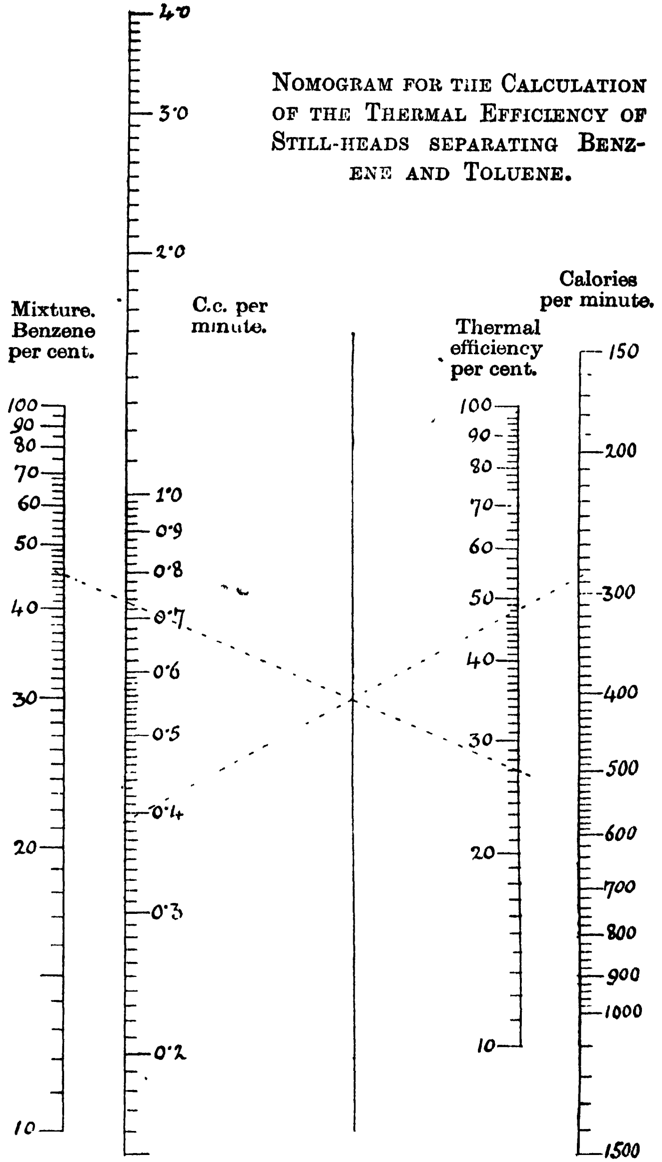
Thermometers reading to 0·1°, calibrated in position by the distillation of pure benzene and pure toluene, indicated the purity of the products. A small window was provided in the jacket to enable the boiling point on the toluene thermometer to be read. This thermometer formed the lowest portion of the core upon which the spiral track was wound.

The still could be regulated by altering the lagging upon the upper half, by adjusting the rate of feeding, and by varying the heat supply.

Tests were made with a 50 per cent. mixture of benzene and toluene, and it was found possible to regulate the still to work automatically, yielding pure benzene and pure toluene continuously, the temperatures indicated on the thermometers not differing by 0·05° from the calibrated temperatures. A rate of feeding of more than 0·5 c.c. per minute was attained.

In one experiment, with a heat supply of 309 calories per minute, pure benzene and pure toluene were collected each at the rate of 0·26 c.c. per minute. The separation of one gram of benzene required, therefore, the expenditure of 1340 calories. As the

FIG. 2.

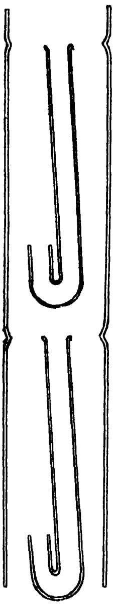


theoretical quantity of heat required is calculated to be 208 calories (A. F. Dufton, *loc. cit.*) the thermal efficiency of the still was 15·5 per cent.

In another experiment with the same still, the lagging upon the upper half of the column was increased. With a rate of heating of 215 calories per minute pure benzene and pure toluene were collected each at the rate of 0·18 c c. per minute. This also corresponds with a thermal efficiency of 15·5 per cent.

Further experiments with this type of column projected with a view to obtain an increased rate of feeding, a higher thermal efficiency, and easier regulation were discontinued, experiments, made concurrently with this investigation, having shown that perfect separation in the laboratory is possible with other types of still-head. Some of the columns used appeared to be better adapted for continuous working than the Dufton column, which was specially designed to have minimum working volume, a matter of paramount importance in the separation of small quantities of liquid, but of no significance at all in continuous working.

FIG. 3.



In testing various still-heads, in a search for a simply constructed column giving with high thermal efficiency a pure product at a high rate of distillation per unit area of section and per unit volume of column, the mixture of benzene and toluene was boiled in a vacuum flask as still. Heat was supplied electrically by means of a coil of wire wound upon mica immersed in the liquid, and the rate of heating was measured by means of a watt-meter. The rate was controlled by means of a rheostat. A thermometer reading to 0·1° placed in the top of the column showed the temperature of the vapour and indicated the purity of the distillate. The thermometer was calibrated in position in the apparatus by the distillation of pure benzene, the boiling point, corrected for variation of atmospheric pressure, being taken as 80·2°. The régime of distillation was so uniform that in one experiment a sudden change in the atmospheric pressure amounting only to 1·2 mm. was inferred from the reading of the thermometer before the reading of the barometer was made.

A nomogram (Fig. 2), constructed from data given in the author's paper in the *Philosophical Magazine*, was used to calculate the thermal efficiency from the rate of distillation, the rate of heating, and the composition of the mixture.

Tables I and II show the results obtained in experiments with a dephlegmator with 50 c.c. of 80 per cent. and 50 per cent. mixtures of benzene and toluene. A constant rate of heating of 287 calories per minute was maintained in each experiment.

The dephlegmator was made in a glass tube 1·5 cm. in diameter and the length of the column was 75 cm. To support the dephlegmating films of liquid, fifteen discs of copper gauze of 80 holes to the inch were sealed to the walls at intervals of 4·5 cm. A glass siphon tube 3 mm. in diameter was fitted through each disc (Fig. 3) to prevent the accumulation of liquid upon the gauze. These tubes acted as traps and prevented the vapour from ascending without bubbling through the liquid. The dephlegmator differed from that of Brown (T., 1880, **37**, 49) in that the latter worked with a layer of liquid 8 mm. deep upon each gauze. Brown, moreover, used copper gauze of 40 mesh, stating that finer gauze would, "of course," mean greater pressure difference between sections. Experiment, however, shows the remarkable fact that the same pressure is required with gauze of 50, 60, or 80 mesh. The pressure required for a mixture of benzene and toluene was 2·5 cm. of liquid and the siphons were made to maintain this pressure.

TABLE I.

Time in minutes.	C.c. collected.	C.c. per min.	Benzene per cent. in the mixture.	Temp.	Thermal efficiency per cent.
0	0·0	—	80	—	—
6	3·3	0·60	79	80·2°	31
12	7·2	0·66	76·5	80·2	35
18	11·3	0·69	74	80·2	37
24	15·5	0·69	71	80·2	38
30	19·6	0·66	67	80·2	37
36	23·4	0·52	62·5	80·2	30
42	25·7	0·36	59	80·2	22
48	27·7	0·29	55	80·2	17
54	29·2	0·21	52	80·2	14
60	30·2	0·14	49·5	80·2	
66	30·9	0·10	47·5	80·2	

TABLE II.

Time in minutes.	C.c. collected.	C.c. per min.	Benzene per cent. in the mixture.	Temp.	Thermal efficiency per cent.
0	0·0	—	50	—	—
7·5	2·1	0·32	46	80·15°	22
15	4·8	0·39	45	80·2	27
22·5	7·9	0·40	41	80·2	29
30	10·7	0·35	36	80·2	27
37·5	13·1	0·30	32	80·2	25
45	15·2	0·22	28	80·2	21
52·5	16·3	0·15	26	80·2	15
60	17·3	0·10	24	80·2	13
67·5	17·8	0·06	22	80·2	
75	18·2	0·05		80·2	
82·5	18·6	0·03		80·2	

Table III shows the results obtained with a still-head made by filling a glass tube 2·3 cm. in diameter and 100 cm. long with thin-walled, cylindrical, glass beads 4 mm. long and 4 mm. in diameter. A mixture of 500 c.c. of benzene with 300 c.c. of toluene was employed and the rate of heating was 1000 calories per minute throughout the experiment.

For a 50 per cent. mixture, the thermal efficiency was 47 per cent.; the rate of distillation was 0·60 c.c. per minute per sq. cm. of cross-section and 6·0 c.c. per minute per litre of still-head. This column is simple to construct, easy to operate, and not liable to become deranged. It appears to possess all the advantages sought for in a column for continuous working.

TABLE III.

Time in minutes.	C.c. collected.	C.c. per min.	Benzene per cent. in the mixture.	Temp.	Thermal efficiency per cent.
0	0	—	62·5	—	—
20	60	2·8	59·5	80·2°	47
40	113	2·7	57	80·2	47
60	165	2·6	53	80·2	47
80	219	2·5	48	80·2	47
100	271	2·4	43	80·2	47
120	314	2·05	38	80·2	45
140	353	1·7	33	80·2	40
160	382	1·4	28	80·2	38
180	408	1·1	23	80·2	33
200	423	0·8	20	80·2	27
220	438	0·7	17	80·2	27
240	451	0·6	14	80·2	27
260	462	0·4	11	80·2	24
280	468	0·3	10	80·2	17

The author desires to express his thanks to the Government Grant Committee of the Royal Society for funds placed at his disposal, which have defrayed part of the cost of this research.

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CCXXIX.—*The Colour of Iron Alum.*

By JANE BONNELL and EDGAR PHILIP PERMAN.

IT is well known to chemists that iron ammonium alum occurs in two distinct forms, namely, the more usual form of a violet colour and also a colourless form. Ostwald put forward the theory that the latter is the pure form, the colour of the other being due to the presence of manganese as an impurity ("Grundlinien der anorganischen Chemie," 1900, 585). This might very easily be the case, and it was with the view of testing the validity of the hypothesis and of investigating the whole question that the following experiments were performed.

1. *Testing the Coloured Variety for Manganese.*—Some of the coloured variety was dissolved in water and the iron precipitated as basic acetate by means of ammonium acetate and acetic acid. This basic acetate was filtered off and thoroughly washed with warm water. The washings were added to the filtrate and the whole was evaporated to small bulk. Ammonium hydroxide was then added, the whole evaporated to dryness, and ignited. If manganese were present, it would be left as manganese oxide. Actually a faint black residue was left, which was tested for manganese by means of the borax bead test. The bead remained colourless both in the oxidising and the reducing flame, showing that the residue did not contain an appreciable quantity of manganese.

2. *Preparation of the Alum by Purifying from Manganese.*—This experiment was performed to test the previous result. Some of the coloured variety was dissolved in water and the iron partly precipitated as basic acetate. This basic acetate was filtered off and thoroughly washed as before. It was then dissolved in dilute sulphuric acid, and the solution divided into two portions, *A* and *B*.

A was converted into the alum. On crystallising, it gave coloured crystals.

In *B*, the iron was again partly precipitated as basic acetate, this basic acetate carefully washed as before, again dissolved in sulphuric acid, and then converted into the alum. This also yielded coloured crystals. It should be noted that both solutions *A* and *B* were strongly acid. Together, experiments 1 and 2 seem to show that the colour was not due to the presence of manganese, but was the colour of the pure salt.

3. *Preparation of Colourless Alum.*—These experiments fall into two divisions :

A. Attempts to prepare the colourless salt from the slightly reduced alum.

B. Attempts to prepare it from alum containing ferric hydroxide.

A. 1. A small quantity of the colourless alum was already available, as it had been prepared by a student in carrying out the preparation of iron alum as a practical exercise. On being tested, this was shown to contain ferrous salt, that is, there had been incomplete oxidation. A portion was oxidised with nitric acid in the presence of sulphuric acid and allowed to crystallise. The solution yielded coloured crystals.

2. Some of the coloured alum was slightly reduced by means of sulphuric acid and iron filings. This solution yielded coloured crystals.

3. Some ferrous sulphate solution was added to a solution of the coloured alum and the whole allowed to crystallise. Coloured crystals were obtained.

Evidently, then, the loss of colour is not due to the presence of ferrous salts.

B. These experiments were based on the hypothesis that the colourless form might be due to the presence of ferric hydroxide.

1. A solution of the coloured alum was treated with a few drops of ammonium hydroxide and left to crystallise, when faintly brown crystals separated out.

2. Equal quantities of the crystals obtained in the previous experiment and of the violet crystals were dissolved together, and the solution was allowed to crystallise. The crystals obtained were still of a brown colour, but in both experiments the crystals showed no trace of the violet coloration of the original crystals.

3. A solution of the coloured alum in water was boiled for about ten minutes, and then allowed to crystallise, when colourless crystals separated out. It is known that solutions of this alum hydrolyse to an appreciable extent when heated, if strongly acid solutions are not used.

4. Some of the colourless crystals obtained were redissolved in water and the solution was made strongly acid. This yielded coloured crystals.

5. A saturated solution in cold water of the coloured alum was prepared and allowed to crystallise. The crystals did not separate out for about fifteen days and were of a mixed character, some being colourless and some having a faintly violet tinge. The colourless crystals were redissolved in cold acid solution and allowed to crystallise, when the violet crystals were obtained.

Conclusion.

These simple experiments point to the fact that the coloured form of the iron ammonium alum is the pure form of the salt. The colourless variety is due to the presence of ferric hydroxide (probably colloidal), the brown colour of which neutralises the colour of the alum itself. It has also been shown that simply boiling a solution of the alum for a few minutes, bringing about hydrolysis of the salt, produces sufficient ferric hydroxide to neutralise the colour, and to make the solution yield colourless crystals, except when strongly acid solutions are used.

In ordinary circumstances, when the alum is being prepared, the solutions are strongly acid, very little hydrolysis takes place, and the coloured form is therefore produced.

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CCXXX.—*The Direct Iodometric Estimation of Lead Peroxide.*

By Samuel Glasstone.

The method of the direct iodometric estimation of lead peroxide (or of red lead) without distillation was first introduced by Diehl (*Dingl. polyt. Journ.*, 1882, **246**, 196). When lead peroxide is acted upon with dilute acid (acetic) in the presence of potassium iodide, the iodine liberated in accordance with the following equation may be directly titrated with standard thiosulphate solution.

$$PbO_2 + 4HI = PbI_2 + 2H_2O + I_2.$$

An excess of ammonium acetate was added in order to keep the lead iodide in solution, as in the solid form it not only interfered with the detection of the end point, but also formed an insoluble coating round the solid peroxide and thus prevented further action. For this reason the acid used in the first place was acetic acid, as any stronger acid would be converted into it.

Topf (*Zeitsch. anal. Chem.*, 1887, **26**, 277) slightly modified the method of Diehl, by using sodium acetate instead of ammonium acetate, and defined the quantities of the various reagents to be used in the estimation.

Reinsch (*Chem. Zentr.*, 1907, i, 993), Marchese (*Gazzetta*, 1907, **37**, ii, 292), Beck (*Zeitsch. anal. Chem.*, 1907, **46**, 456), and Milbauer (*Chem. Zeit.*, 1909, **33**, 522) modified the Topf-Diehl method by varying the quantities of the substances used in the reaction.

Chwala and Colle (*Zeitsch. anal. Chem.*, 1911, **50**, 209) examined the various modifications of this method and showed that uncertain results are caused by (*a*) the action of iodine on lead salts in the presence of acetic acid, resulting in the formation of methyl iodide, methyl acetate, and iodoacetic acid, and (*b*) the reversible reaction $6H^{\cdot} + 5I' + IO_3' \rightleftharpoons 3I_2 + 3H_2O$ (Sammet, *Zeitsch. physikal. Chem.*, 1905, **53**, 642), which prevents an appreciable amount of the iodine liberated by the lead peroxide from being titrated by thiosulphate.

Milbauer and Pivnicka (*Zeitsch. anal. Chem.*, 1914, **53**, 345) made a fairly complete investigation of the various factors involved in the Topf-Diehl reaction, and obtained the following results: (*a*) the effect of time was to diminish the amount of "titratable" iodine formed, for example, when the results obtained were calculated as percentages of PbO_2, the value obtained after ten minutes was 90·28, after twelve minutes, 89·6, and after sixty minutes, 86·0; (*b*) at higher temperatures (up to 60°) lower results were obtained, (*c*) 50 per cent. acetic acid gave a higher result than 5 per cent. acetic acid, (*d*) dilution to 200 c.c. gave higher results than dilution to 20 c.c., and (*e*) potassium and sodium acetates gave higher results than an equivalent amount of ammonium acetate. As a consequence of these investigations, the authors laid down conditions for the estimation of lead peroxide by this method; a glance at their experimental results, however, shows that the method cannot be regarded as by any means quantitative.

A further disadvantage of the Topf-Diehl method mentioned by Reinders and Hamburger (*Zeitsch. anorg. Chem.*, 1914, **89**, 71) is the very slow rate of solution of the lead peroxide (or red lead) in the acetic acid mixture.

The object of this work was to find the conditions under which the interaction of lead peroxide and hydriodic acid would give quantitative and reproducible results. It seemed possible that a source of error, in addition to those given by Chwala and Colle (*loc. cit.*), might be the appreciable reversibility of the reaction,

$$PbO_2 + 4HI \rightleftharpoons PbI_2 + 2H_2O + I_2$$

(compare the similar reaction with hydrochloric acid, Wescott, *J. Amer. Chem. Soc.*, 1920, **42**, 1335), and an experiment was arranged to test this possibility. If the conditions in the reaction are such that lead peroxide and lead iodide are solid phases, and the solution is moderately dilute, we should have, in the aqueous layer, $[HI]^4/[I_2]$ = a constant at a definite temperature.

EXPERIMENTAL.

A mixture of a large excess of lead peroxide and 20 c.c. of approximately *N*-hydrochloric acid containing 6 grams of potassium iodide was placed in a thermostat at 25°, and well shaken from time to time. After definite intervals, a known volume of the clear liquor was withdrawn, diluted, and rapidly titrated with *N*/10-thiosulphate, and then with *N*/10-sodium hydroxide.

Time.	C.c. of $N/10$-thiosulphate (a).	C.c. of $N/10$-NaOH (b).	$2a + b$.
30 mins.	8·1	3·0	19·2
60 ,,	9·4	0·4	19·2
180 ,,	9·6	nil	19·2
24 hours	9·6	nil	19·2

The results show that the reaction is not reversible to any appreciable extent, since all the hydrogen ions (as nearly as could be volumetrically determined) had been used up.

The uncertain results obtained in the Topf-Diehl method can be attributed only to the action of iodine on acetates and the formation of iodate (Chwala and Colle, *loc. cit.*). Both these sources of error would be eliminated by the use of hydrochloric acid instead of acetic acid, provided a means could be found of keeping the lead iodide in solution. The hydrogen-ion concentration would then be so great as to force the equilibrium in the iodate–iodide–iodine reaction well over to the free iodine side; for example, iodate may be estimated by adding acidified potassium iodide solution, and titrating the iodine quantitatively liberated. A further advantage in using hydrochloric acid would be the more rapid solution of the sample under analysis.

Solution of the Lead Iodide.

Sutton ("Volumetric Analysis," 10th ed., p. 138) and Schimpf ("Manual of Volumetric Analysis," 5th ed., p. 222) describe a method for estimating lead peroxide by digestion with hydrochloric acid and potassium iodide in a tightly stoppered bottle placed in a boiling-water bath. By this method the lead iodide is kept in solution during the course of the reaction (due to the elevated temperature), but the sparingly soluble salt separates out on cooling previous to titration. Milbauer and Pivnicka (*loc. cit.*) showed that a large excess of potassium iodide (40 grams for 0·2 gram of lead peroxide) kept the lead iodide in solution; this method is much too expensive.

The well-known solubility of lead haloids in solutions of alkali haloids led to the trial of sodium chloride; it was found that the presence of the latter salt greatly increased the solubility of lead iodide. Even in the presence of fairly concentrated hydrochloric acid, when the amount of sodium chloride in solution was greatly reduced, the solubility of the lead iodide was still considerable.

Concentration of the Acid.

The proposed method of estimation was to digest a weighed amount of lead peroxide (or red lead) with hydrochloric acid at room temperature in the presence of potassium iodide and a large excess of sodium chloride. The effect of variation in the acid concentration on (*a*) the amount of iodine liberated, and (*b*) the rate of solution of the lead oxide and iodide, due to the corresponding alteration in the solubility of the sodium chloride, had to be determined. A series of experiments was arranged in which a definite weight of lead peroxide (0·2 gram) was added to 100 c.c. of hydrochloric acid varying in concentration from $N/2$ to $5N$, containing 1 gram of potassium iodide and excess (about 30 grams) of sodium chloride. The time for complete solution of the peroxide was roughly noted in each case and the iodine titrated against thiosulphate solution. The titrations were identical in each case, but when the hydrochloric acid was about $2N$, the rate of solution appeared to be greatest. This concentration, although not essential, was finally adopted for subsequent work. The amount of potassium iodide used in this process was always somewhat greater than that required by theory, owing to the sparing solubility of iodine in water. The iodide used must, of course, be free from iodate.

The effect of time on the amount of titratable iodine was also investigated; after three hours the titration was the same as that in a similar experiment in which the iodine had been titrated immediately.

In order to promote dissolution of the lead oxide, which in any case was far more rapid than in the Topf-Diehl method, the oxide was very finely ground, and the reaction carried out in a stoppered bottle which could be vigorously shaken. Under these conditions, no difficulty was ever experienced in getting specimens into solution.

These experiments showed that the direct iodometric estimation of lead peroxide could be put on a much better foundation than that of the Topf-Diehl method. The following procedure was then adopted for quantitatively estimating lead peroxide.

Method of Analysis.

Lead peroxide (0·2 gram) or red lead (0·5 gram) was weighed out into a bottle containing 20 c.c. of 36 per cent. hydrochloric acid, 100 c.c. of water, 20 to 25 grams of sodium chloride, and about 1 gram of potassium iodide. The bottle was stoppered and the whole well shaken for one or two minutes to ensure complete solution of the lead oxide. The liberated iodine was titrated with $N/20$-thiosulphate solution, starch being added towards the end of the reaction. Very satisfactory duplicate results were obtained in this way. Owing to the uncertain results obtained by other methods of estimating lead peroxide (for a summary of these, see Chwala and Colle, *loc. cit.*), this method was checked by the estimation of lead in a pure lead salt (see below).

Small amounts of nitrate (a possible impurity in lead peroxide and in red lead) had no effect on the amount of iodine liberated.

The method described was also applied to the general estimation of lead, use being made of the oxidation of lead in boiling alkaline solution to lead peroxide by means of bromine water. A definite quantity of the lead salt was dissolved in water or in 5 per cent. sodium hydroxide solution; in either case alkali was added until the lead hydroxide had completely dissolved. Excess of bromine water was then added, and the mixture kept at or near the boiling point for some time (one to two hours) completely to convert the lead sesquioxide first formed into the peroxide, otherwise low results were obtained. The peroxide was then filtered off while hot and washed with boiling water (cold water gives colloidal filtrates) until free from bromine or hypobromite (test with acidified potassium iodide and starch). To ensure complete oxidation to peroxide, the precipitate may be digested with hot dilute acetic acid, and the filtrate made alkaline and again treated with bromine water. The filter-paper and contents were then placed in a bottle containing suitable quantities of hydrochloric acid, sodium chloride, and potassium iodide, for example, those recorded above. The bottle was well shaken to disintegrate the filter-paper, the contents were diluted with water and titrated with thiosulphate of suitable concentration. In this way results in agreement with the gravimetric estimation of lead as sulphate were obtained. This method is particularly useful in the case of very dilute solutions of lead salts where the gravimetric method is inapplicable; for example, 10 c.c. of a solution containing less than 0·004 gram of lead was easily analysed by this volumetric method.

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CCXXXI.—*The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part III. Products Derived from Halogenated Glutaconic Acids.*

By ERNEST HAROLD FARMER and CHRISTOPHER KELK INGOLD.

IT has been stated (this vol., p. 951) that the principal points in which Baeyer's Spannungstheorie is at variance with the known facts of organic chemistry fall into two classes, the first consisting of those which relate to the effect on ring formation of the number of carbon atoms composing the ring, and the second those relating to the influence of substituent groups.

In the previous papers on this subject (this vol., pp. 305, 951) a series of definitely comparative experiments has been described by means of which, it is hoped, the precise extent of discrepancies of both types can be gauged with some degree of certainty. Such a series of experiments, if sufficiently extended, must in the end yield the information required for a restatement in more exact form of the fundamental conditions which underlie the formation and fission of carbon rings, and lead to a clearer comprehension of the reason for the fact that the tendencies to ring-formation and to fission are not strictly reciprocal properties; already, however, it has been noticed that many of the more obvious defects of the "Spannungstheorie," defects emerging, not only from *ad hoc* experiments, but also from a general survey of the literature of synthetic and naturally occurring carbocyclic compounds, disappear if the modifying hypothesis be made that groups attached to a carbon atom will, when not involved in ring formation, assume positions determined by their respective volumes relative to one another and to the available space.

The method employed in the experiments referred to, namely, measuring the extent to which ring formation occurs in competition with a uniform side reaction under standard experimental conditions, has been previously described (*loc. cit.*) in some detail, and, in view of the fact that the underlying hypothesis is capable of being expressed to a first approximation in a quantitative form, every effort has been and is being made to obtain all the accuracy of which the method is capable. In this way (compare Parts I and II) the formation of *cyclo*propane derivatives from *n*-propane compounds and of analogous *cyclo*butane derivatives from *n*-butane compounds has already been studied, and at the present time the investigation is being extended both to other types of ring and to rings containing substituents varying in number, position, and in kind. In the meantime, however, it seemed desirable to bring within the ambit of the investigation the study of a third influence regarding which very little precise information is at present available, namely, the influence of unsaturation on the formation of cyclic compounds.

At the outset difficulty was experienced in selecting for investigation a suitable unsaturated acid capable of being treated according to the method used in the preceding parts of the research and at the same time having some claim to be regarded as a typical substance; for an examination of such information as exists indicated that totally different effects would be observed when dealing with unsaturated compounds having differently situated double bonds. Since, however, in Parts I and II (*loc. cit.*) the open-chain substances employed were glutaric and adipic acids (I and II), it was ultimately decided to examine in a similar manner and under comparable conditions the corresponding unsaturated derivatives, namely, glutaconic and muconic acids (III and IV), although there can be no question but that neither of these acids can be regarded as a normal unsaturated substance.

$$\mathrm{CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H} \qquad \mathrm{CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$$

(I.) (II.)

$$\mathrm{CO_2H{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H} \qquad \mathrm{CO_2H{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H}$$

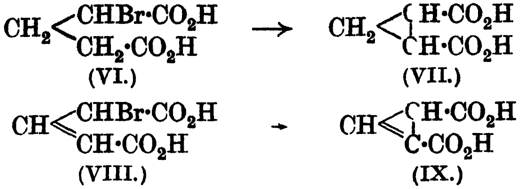
(III.) (IV.)

$$\mathrm{CO_2H{\cdot}\underset{\bullet}{C}H{\cdot}CH_2{\cdot}\underset{\bullet}{C}H{\cdot}CO_2H}$$

(V.)

It is unnecessary to refer, except in the briefest manner, to the extended researches of Thorpe and his collaborators into the chemistry of the glutaconic acids. The clear outcome of this investigation has been that glutaconic acid is no ordinary unsaturated acid, and that, whilst it still possesses, although in greatly diminished degree, the characteristics of an unsaturated compound of the formula III, it has, in addition, another series of properties which this formula does not express and which suggest both symmetry of constitution and a condition of 1 : 3-unsaturation. The explanation offered is that the stable form of glutaconic acid has the "semi-aromatic" formula (V) (the "free" 1 : 3-valencies being associated sufficiently to limit to some extent the tendency towards 1 : 3-addition), but that in most experiments with the acid the unsaturated form (III) is present in small amount in a condition of tautomeric equilibrium. Many facts support this hypothesis. Nevertheless, it cannot be denied that in adopting such a formula for glutaconic acid one tacitly accepts the view that the chemistry of this substance consists largely of phenomena to which the ordinary three-dimensional formulæ-models can give no clue, and from this point of view the behaviour of glutaconic acid and its derivatives in relation to the requirements of the "Spannungstheorie" (which depends essentially on the tetrahedral carbon model) appears to possess more than ordinary interest.

Comparing, for instance, the formation of *cyclo*propane-1 : 2-dicarboxylic acid (VII) from α-bromoglutaric acid (VI) with the formation of Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid (IX) from α-bromoglutaconic acid (VIII) by the elimination of hydrogen bromide in each case, one observes that the unsaturated cyclic acid should be



$$CH_2<\begin{matrix}CHBr\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix} \longrightarrow CH_2<\begin{matrix}CH\cdot CO_2H\\ |\\ CH\cdot CO_2H\end{matrix}$$

(VI.) (VII.)

$$CH\leqslant\begin{matrix}CHBr\cdot CO_2H\\ CH\cdot CO_2H\end{matrix} \rightarrow CH\leqslant\begin{matrix}CH\cdot CO_2H\\ |\\ C\cdot CO_2H\end{matrix}$$

(VIII.) (IX.)

considerably the more difficult to produce, the formation numbers (*loc. cit.*) in these instances being 0·345 and 0·385 respectively. Another factor, however, must be taken into account; for in all experiments of this kind it is essential to have some guarantee that the effects attributed to differing tendencies towards ring closure are not being masked by the differing reactivities of the halogen compounds employed. Indeed this consideration constitutes the main reason for employing the standard side-reaction method, since by this means any serious difference in the reactivities of the halogen compounds is immediately detected, and, in fact, is largely (although, in all probability, not exactly) compensated. The case with which we are here dealing furnishes the first instance so far met with in the course of these investigations of a halogen compound differing in reactivity from the analogues previously employed. The point of importance, however, is that the difference in this case is in the sense which again indicates that greater difficulty will attend the formation of the unsaturated ring acid (IX) than of the saturated acid (VII).

On two counts, therefore, the *cyclo*propenedicarboxylic acid should be less easily produced, but it will be a matter for surprise to no one prepared to regard α-bromoglutaconic acid as a " semi-aromatic " substance (X) having 1 : 3-valencies in an equilibrium

$$CO_2H\cdot\underset{\bullet}{C}Br\cdot CH_2\cdot\underset{\bullet}{C}H\cdot CO_2H$$

(X.)

state of limited mutual association that, as a matter of fact, the *cyclo*propenedicarboxylic acid is produced considerably more smoothly than its saturated analogue under experimental conditions involving minimal complications in each case.

It is necessary at this stage, in order to render intelligible the significance of some of the factors which complicated the series of reactions from the products of which the *cyclo*propenedicarboxylic acid was isolated, to indicate the method by which the bromo-acid (X), or rather one of its esters, was obtained for the investigation. As Feist has shown (*Ber.*, 1911, **44**, 135), ethyl glutaconate readily absorbs two atoms of bromine and yields a dibromo-ester (XI). This substance, when treated with diethylaniline under the conditions described in the experimental part of this paper, yields ethyl bromoglutaconate (XII), in which the position of the bromine atom is clearly proved by the nature of the products formed on complete hydrolysis. The free dibromo-acid (XIII) was prepared by

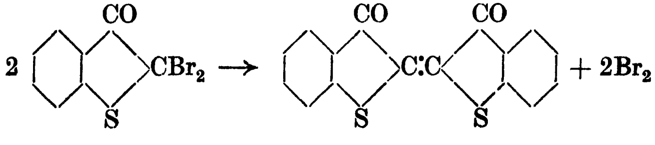
$$CO_2Et\cdot CH_2\cdot CHBr\cdot CHBr\cdot CO_2Et \quad \text{(XI.)}$$

$$CO_2Et\cdot \underset{\bullet}{C}Br\cdot CH_2\cdot \underset{\bullet}{C}H\cdot CO_2Et \quad \text{(XII.)}$$

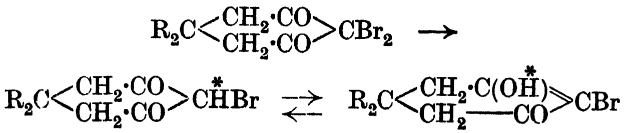
$$CO_2H\cdot CH_2\cdot CHBr\cdot CHBr\cdot CO_2H \quad \text{(XIII.)}$$

Verkade and Coups (*Rec. trav. chim.*, 1920, **39**, 586) by the action of bromine vapour on glutaconic acid in the absence of a solvent, but on attempting to prepare α-bromoglutaconic acid from this substance by elimination of hydrogen bromide, unexpected difficulties were experienced. Many experiments were made with a view to discover the correct conditions, but although indications were obtained that the monobromo-acid (X) was actually produced in considerable amount, it always appeared to be accompanied either by unchanged dibromide or by products of further decomposition, which, owing to the labile character of the bromine in the monobromo-acid, rendered purification exceedingly difficult. Since, therefore, after repeated attempts a satisfactory specimen was not obtained, the complete hydrolysis by alkalis of the dibromo-acid (XIII) was investigated under the usual two sets of standard experimental conditions in the hope that the character of the products would indicate the intermediate formation of the bromo-acid which it had not been possible to purify. This assumption proved in the main to be correct.

Nevertheless, when the dibromide was hydrolysed, certain reactions were observed which were not met with when the monobromo-ester was employed. Probably the most remarkable of these was that by which, under the influence either of concentrated or of dilute alkali, glutaconic acid (V) was produced with the elimination, not of hydrogen bromide, but of bromine, a type of reaction to which comparatively few parallels are known. However, those instances which have been recorded of the elimination of a halogen as such, either spontaneously or by some reagent (other than a reducing agent), are certainly to be regarded as indicating an exceedingly strong tendency towards formation of the product obtained. Thioindigotin, for example, is produced by merely heating 1 : 1-dibromo-2-ketodihydrothionaphthen (Bezdzik, Friedländer, and Koeniger, *Ber.*, 1908, **41**, 234), whilst several cases of the passage



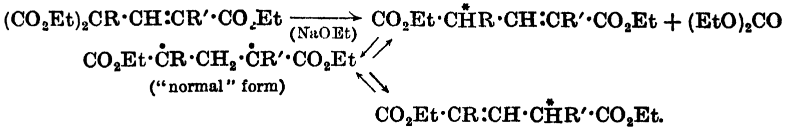
of the dibromo-derivative of a dihydroresorcinol into the corresponding monobromo-compound by the action of aqueous alkalis alone have quite recently been investigated (Norris and Thorpe, this vol., p. 1209–1210) :



$$R_2C<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>CBr_2 \longrightarrow$$

$$R_2C<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>\overset{*}{C}HBr \rightleftarrows R_2C<\begin{matrix}CH_2\cdot C(O\overset{*}{H})\\ CH_2\text{——}CO\end{matrix}>CBr$$

In the latter case, the great ease of formation of the product is almost certainly to be connected with the well-known tendency to acquire the mobile hydrogen atom (marked *) possessed by a potentially tautomeric system, a tendency well illustrated by the remarkable facility with which a carbethoxyl group is eliminated as ethyl carbonate from substituted glutaconic esters of the type $(CO_2Et)_2CR\cdot CH{:}CR'\cdot CO_2Et$ by the action of cold sodium ethoxide :



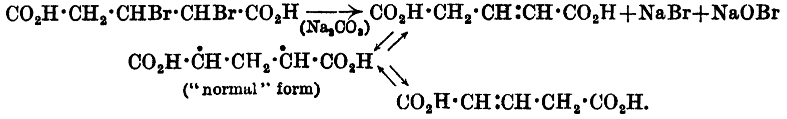
$$(CO_2Et)_2CR\cdot CH{:}CR'\cdot CO_2Et \xrightarrow[(NaOEt)]{} CO_2Et\cdot\overset{*}{C}HR\cdot CH{:}CR'\cdot CO_2Et + (EtO)_2CO$$

$$CO_2Et\cdot\dot{C}R\cdot CH_2\cdot\dot{C}R'\cdot CO_2Et \rightleftarrows$$

("normal" form)

$$CO_2Et\cdot CR{:}CH\cdot\overset{*}{C}HR'\cdot CO_2Et.$$

Once the mobile hydrogen atom (marked *) is obtained, the system becomes tautomeric and shows no further tendency to break down until interchange with the " normal " (semi-aromatic) form is again suppressed by replacing the hydrogen atom by an alkyl group (Thole and Thorpe, T., 1911, **99**, 2187). The formal similarity with the hydrolytic reaction mentioned above is obvious :



$$CO_2H\cdot CH_2\cdot CHBr\cdot CHBr\cdot CO_2H \xrightarrow[(Na_2CO_3)]{} CO_2H\cdot CH_2\cdot CH{:}CH\cdot CO_2H + NaBr + NaOBr$$

$$CO_2H\cdot\dot{C}H\cdot CH_2\cdot\dot{C}H\cdot CO_2H \rightleftarrows$$

("normal" form)

$$CO_2H\cdot CH{:}CH\cdot CH_2\cdot CO_2H.$$

Now the whole difference between the stability of three-carbon systems and that of tautomeric systems of other types is one of symmetry (Ingold and Thorpe, this vol., p. 492), the permanence of the " normal " forms being dependent on this more than on any other separate factor. The normal form of glutaconic acid itself, therefore, is at once the most mobile in its dynamic and the most stable in its equilibrium relations with its unsaturated isomeride, of any normal acid of the series; hence it seems plain that the effect of molecular symmetry on three-carbon tautomerism is the ultimate cause to which the remarkable tendency towards the production of glutaconic acid, even by abnormal reactions such as the elimination of bromine from αβ-dibromoglutaric acid and of nitrogen from esters of pyrazole-3 : 5-dicarboxylic acid (compare p. 2009), is to be attributed.

The glutaconic acid obtained in these experiments was invariably accompanied by β-hydroxyglutaric acid (XIV), which was evidently a secondary product formed by the addition of the elements of water to the unsaturated form of glutaconic acid (III) during the process of isolation. Verkade has shown (*K. Akad. Wetensch. Amsterdam*, 1915, **18**, 981) that glutaconic acid unites with water in this manner when an acid solution is evaporated, whilst Fichter and Dreyfus (*Ber.*, 1900, **33**, 1452) proved that the reverse reaction proceeds in the presence of alkalis; hence the change is probably

$$CO_2H{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H + H_2O \rightleftarrows$$
$$CO_2H{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H \quad \text{(XIV.)}$$

to be regarded as reversible, the equilibrium depending on the extent to which the end-products undergo further change under the conditions employed. Our observations on the matter appear to indicate that the principal circumstance affecting the equilibrium is the conversion in acid solution of the hydroxy-acid into a β-lactone or a lactide, which, however, is unstable and difficult to isolate.

Another acid the formation of which was observed in experiments on the action of alkalis on αβ-dibromoglutaric acid was αβ-dihydroxyglutaric acid, the product of complete hydroxylation * (XV). As with most hydroxylation products formed by similar methods, the quantity obtained (*vide* Tables I and II, p. 2011) was particularly large when dilute alkalis were employed for the hydrolysis.

$$CO_2H{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H \quad \text{(XV.)}$$

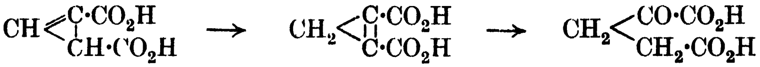
Regarding the substances obtained from ethyl monobromoglutaconate or from the monobromo-acid formed intermediately in the hydrolysis of αβ-dibromoglutaric acid, it will immediately be obvious that the final hydroxylation product to be expected is α-ketoglutaric acid (XVIII), into which α-hydroxyglutaconic acid (XVI) must be converted (*via* its unsaturated modification, XVII) almost at the moment of its formation :

$$\underset{\text{(XVI.)}}{CO_2H{\cdot}\dot{C}(OH){\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2H} \longrightarrow \underset{\text{(XVII.)}}{CO_2H{\cdot}C(OH){:}CH{\cdot}CH_2{\cdot}CO_2H} \longrightarrow$$
$$\underset{\text{(XVIII.)}}{CO_2H{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$$

---

* Kiliani and Loeffler (*Ber.*, 1905, **38**, 3624) obtained this substance in small yield both by the action of permanganate on glutaconic acid and by boiling the acid in an aqueous solution to which the theoretical amount of bromine (two atoms) had been added. The latter observation is of interest, because *αβ*-dibromoglutaric acid has never been obtained from the product formed by the action of bromine on glutaconic acid in the presence of water, or, indeed, of any other solvent (Thorpe, T., 1919, **115**, 679).

Actually, this keto-acid invariably constituted a considerable proportion of the product obtained whether concentrated or dilute alkalis were employed in the hydrolysis. This relatively slight difference, well illustrated by the figures recorded in Tables I and III (pp. 2011, 2012), between the quantities produced under the two sets of standard experimental conditions (one involving the use of 2*N*-aqueous sodium carbonate, the other of 6*N*-methyl alcoholic potassium hydroxide) which have been employed throughout this as well as in the preceding parts of the investigation, appeared the more unaccountable when considered in relation to the large differences obtained in other cases (*loc. cit.*), until it was suspected that α-ketoglutaric acid was the ultimate product of two distinct series of reactions. That this was really the case was satisfactorily proved by direct experiment; for it was found that the *cyclo*-propenedicarboxylic acid (IX), although quite stable to dilute aqueous sodium carbonate, was decomposed somewhat readily by concentrated methyl-alcoholic potassium hydroxide forming amongst other products a considerable proportion of α-ketoglutaric acid. The reaction probably involves the transposition of the cyclic double bond followed by ring fission, and may be formulated as follows :

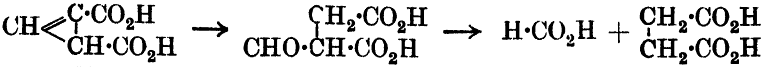


$$\mathrm{CH}\Big\langle\begin{array}{l}\mathrm{C{\cdot}CO_2H}\\ \mathrm{CH{\cdot}CO_2H}\end{array} \longrightarrow \mathrm{CH_2}\Big\langle\begin{array}{l}\mathrm{C{\cdot}CO_2H}\\ \mathrm{C{\cdot}CO_2H}\end{array} \longrightarrow \mathrm{CH_2}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CO_2H}\end{array}$$

(IX.) (XIX.) (XVIII.)

Plainly, therefore, whilst the whole quantity of the keto-acid obtained from the products of the hydrolyses by sodium carbonate is to be regarded as representing the extent to which hydroxylation occurred in these instances, the same inference cannot be drawn in connexion with the experiments in which methyl-alcoholic potassium hydroxide was employed, since a considerable proportion of the ketoglutaric acid produced in these cases must have been formed by the fission of the *cyclo*propene derivative (XIX).

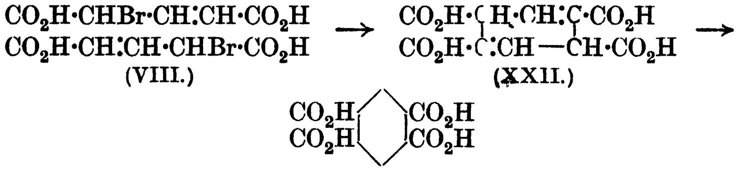
A second substance formed by the hydrolytic decomposition of the *cyclo*propenedicarboxylic acid (IX) was succinic acid (XXI), which was always present in small amount in the products obtained when methyl-alcoholic potassium hydroxide was used. Obviously this acid must be formed by the fission of the *cyclo*propenedicarboxylic acid *without* previous migration of the double bond, aconic acid (XX) being intermediately produced :



$$\mathrm{CH}\Big\langle\begin{array}{l}\mathrm{C{\cdot}CO_2H}\\ \mathrm{CH{\cdot}CO_2H}\end{array} \longrightarrow \begin{array}{r}\mathrm{CH_2{\cdot}CO_2H}\\ \mathrm{CHO{\cdot}CH{\cdot}CO_2H}\end{array} \longrightarrow \mathrm{H{\cdot}CO_2H} + \begin{array}{l}\mathrm{CH_2{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CO_2H}\end{array}$$

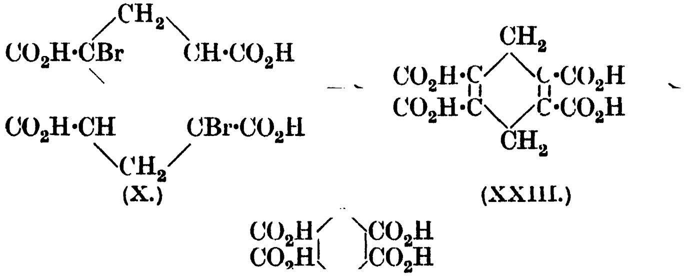
(IX.) (XX.) (XXI.)

It is necessary now to refer to a reaction of a totally distinct type, a reaction, moreover, which appears to constitute a notable addition to the evidence already adduced that the abnormalities which characterise the transformations described in this paper are to be traced to the "semi-aromatic" character of the glutaconic acid derivatives employed. The final product of the change referred to is pyromellitic acid (XXIV), which has previously been obtained by Feist (*Ber.*, 1911, **44**, 135) from ethyl αβ-dibromoglutarate, and in our experiments sometimes formed as much as 30 per cent. of the identified material (Tables I and III, pp. 2011, 2012). Now there is, of course, no difficulty in formulating the production of the dihydro-derivative (XXII) of pyromellitic acid (which obviously must be regarded as the primary product) from two molecules of the unsaturated modification of α-bromoglutaconic acid:



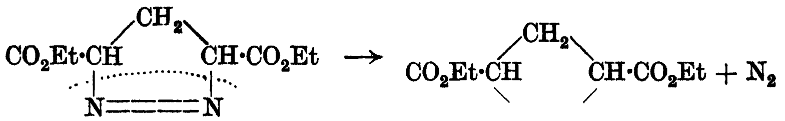
(VIII.) (XXII.) (XXIV.)

There are, however, many difficulties attending this interpretation. It is not clear, for instance, why not even a trace of pyromellitic acid is formed when αγ-dibromoglutaric acid is treated with alkalis under similar experimental conditions. If, however, the conception of limited 1 : 3-unsaturation, well grounded, as we believe, in the cases of glutaconic and β-methylglutaconic acids (Ingold and Thorpe, *loc. cit.*; Thorpe, *loc. cit.*), be extended to the α-bromo-derivative, then the formation of the aromatic acid appears to follow as an almost necessary corollary:



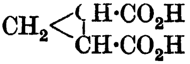
(X.) (XXIII.) (XXIV.)

It may be remarked that this instance of the entrance of a "semi-aromatic" glutaconic acid derivative into the production of a larger ring is in some respects the counterpart of the formation of glutaconic ester (along with *cyclo*propane derivatives) by the elimination of nitrogen from ethyl pyrazole-3 : 5-dicarboxylate (Büchner, *Ber.*, 1890, **23**, 703; *Annalen*, 1893, **273**, 238):

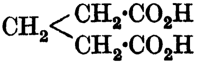


and that together these reactions indicate the degree of stability of the condition of partial association in which the "free" valencies of glutaconic acid are involved.

Finally, it is necessary to trace the history of the two atoms of hydrogen eliminated from the dihydropyromellitic acid (XXIII), and a reference to the tables (pp. 2011, 2012) will make it apparent that they are accounted for, at any rate largely, by the formation of reduction products, namely the *cis*- and *trans*-forms of *cyclo*propane-1 : 2-dicarboxylic acid (XXV) and glutaric acid (XXVI). One or both modifications of the former, evidently arising by reduction of the *cyclo*propenedicarboxylic acid (IX), were obtained from the products of all experiments in which the *cyclo*propenedicarboxylic acid itself was isolated. Glutaric acid, on the other hand, was obtained only in small amount in those experiments in which αβ-dibromoglutaric acid was employed and in which, therefore, glutaconic acid was one of the substances formed.



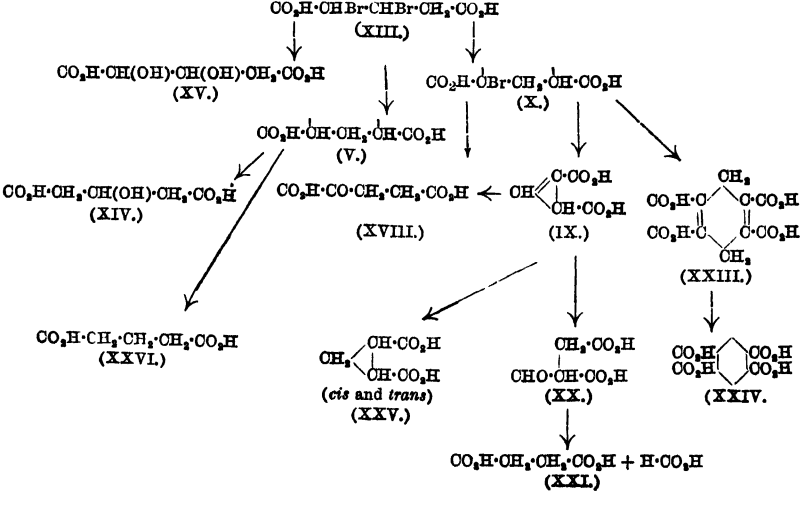
(XXV.)



$$CH_2<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

(XXVI.)

The relationships between the various substances obtained by alkaline hydrolysis of αβ-dibromoglutaric acid and α-bromoglutaconic acid (or ester) are summarised for convenience in the following diagram:



With regard to the quantitative aspect of the investigation, it must at once be admitted that owing to difficulties of separation scarcely more than 60 per cent. at most of the material employed was accounted for as pure products in any single experiment, and that for this reason the numbers obtained cannot be considered as numerically accurate expressions of the facts. Regarded broadly, however, they certainly do admit of some important generalisations.

The quantities of the various products isolated were as follows :—

TABLE I.

	αβ-Dibromoglutaric acid (XIII).		Ethyl α-bromoglutaconate (XII).	
	Dilute alk. (2*N*-aq. Na_2CO_3).	Conc. alk. (6*N*-KOH in MeOH).	Dilute alk. (2*N*-aq. Na_2CO_3).	Conc. alk. (6*N*-KOH in MeOH).
αβ-Dihydroxyglutaric acid (XV)	26	4		
Glutaconic acid (V)	2	5		
β-Hydroxyglutaric acid (XIV)	4	7		
Glutaric acid (XXVI) ...	trace (?)	2		
α-Ketoglutaric acid (XVIII)	20	14	36	20
*cyclo*Propenedicarboxylic acid (IX)	4	2	6	3
*trans-cyclo*Propanedicarboxylic acid (XXV) ...	2	6	5	9
*cis-cyclo*Propanedicarboxylic acid (XXV) ...	0	1	0	4
Succinic acid (XXI) ...	0	2	0	5
Pyromellitic acid (XXIV)	3	10	7	17
Total isolated and identified	61	53	54	58%

From these figures it will be seen that, so far as can be judged from the amounts of identified material, the three simultaneous modes of decomposition of αβ-dibromoglutaric acid occur, under the two standard sets of experimental conditions, to the extents indicated in Table II, from which it is apparent that the formation of glutaconic acid is favoured by the use of concentrated alkalis, whilst the production of the hydroxy-acid takes place, as is usual, most smoothly under conditions of considerable dilution.

TABLE II.

	αβ-Dibromoglutaric acid (XIII).	
	Dilute alk.	Conc. alk.
αβ-Dihydroxyglutaric acid	43	9
Glutaconic acid and substances derived from it	10	25
Substances derived from α-bromoglutaconic acid	57	66
	per cent. of identified material.	

Finally, we may group the substances derived from α-bromoglutaconic acid or its ester into three heads according to the primary decompositions, hydroxylation, *cyclo*propene-ring-formation, *cyclo*-hexadiene-ring-formation, from which they are derived, obtaining in this way Table III; in reading which it must be remembered that for reasons explained on p. 2008 an unknown fraction of the whole quantity of α-ketoglutaric acid obtained from experiments in which concentrated alkali was used is to be attributed to the decomposition of the *cyclo*propenedicarboxylic acid (IX), and that, since α-ketoglutaric acid is also the hydroxylation product of α-bromoglutaconic acid, the figures entered represent only an upper limit to the degree in which this type of decomposition occurs, whilst, similarly, the figures given for *cyclo*propene ring-formation denote merely a lower limit to the extent of its actual occurrence.

TABLE III.

	α-Bromoglutaconic acid.		α-Bromoglutaconic ester.	
	Dilute alk.	Conc. alk.	Dilute alk.	Conc. alk.
α-Ketoglutaric acid	69	40	67	34
*cyclo*Propenedicarboxylic acid and products (other than α-ketoglutaric acid) derived from it	21	32	20	37
Pyromellitic acid	10	28	13	29

per cent. of identified material.

The similarity between the figures referring to α-bromoglutaconic acid and its ester is rendered very obvious in Table III, and furnishes both a justification of the method adopted in studying the reactions of the bromo-acid, and a basis for the conclusion that the carboxyl groups probably play no very essential part in the series of changes observed. The figures which are not subject to the corrections mentioned in the preceding paragraph (that is, those in the first and third columns) are in particularly close agreement and by contrast with the results obtained in Part I (*loc. cit.*) constitute the grounds for the suggestion made on pp. 2003 and 2009 that the formation both of the three-carbon and six-carbon rings is in this instance to be attributed to a condition of limited 1 : 3-unsaturation pre-existing in the open-chain substances employed.

The investigation of the products derived from muconic acid is not yet complete and it is proposed to reserve the description of these for a future communication.

EXPERIMENTAL.

(A) *Halogen Derivatives of Glutaconic Acid.*

The αβ-dibromoglutaric acid required for this investigation was prepared from glutaconic acid by Verkade's bromine-vapour method (*loc. cit.*) and was purified by crystallisation from anhydrous formic acid. Experiments made with the object of obtaining from it α-bromoglutaconic acid by elimination of hydrogen bromide were attended only with a limited degree of success, and ultimately the dibromoglutaric acid itself was subjected to complete hydrolysis by alkalis as described in sections B and C.

The ethyl αβ-dibromoglutarate required for the preparation of ethyl α-bromoglutaconate (below) was obtained from ethyl glutaconate as described by Feist (*loc. cit.*).

Ethyl α-Bromoglutaconate (XII).

Slightly more than the theoretical quantity of diethylaniline was heated nearly to the boiling point and then quickly mixed with ethyl dibromoglutarate. If the materials were quite pure and the operation successful, the product was almost colourless and the neutral oil obtained from it by washing with dilute hydrochloric acid yielded on distillation almost the theoretical amount of ethyl α-bromoglutaconate, a colourless oil, b. p. 140—143°/10 mm. (Found: $C = 40{\cdot}6$; $H = 4{\cdot}9$; $Br = 30{\cdot}0$. $C_9H_{13}O_4Br$ requires $C = 40{\cdot}7$; $H = 4{\cdot}9$; $Br = 30{\cdot}2$ per cent.).

The action of dilute and of concentrated alkalis on this substance is described in sections D and E.

(B) *Action of Dilute Alkalis on αβ-Dibromoglutaric Acid: Formation of αβ-Dihydroxyglutaric Acid, Glutaconic Acid, β-Hydroxyglutaric Acid, α-Ketoglutaric Acid, Δ^2-*cyclo*Propene-1 : 2-dicarboxylic Acid,* trans-cyclo*Propane-1 : 2-dicarboxylic Acid, and Pyromellitic Acid.*

Fifty grams of αβ-dibromoglutaric acid (section A) were boiled with 500 c.c. of 2*N*-aqueous sodium carbonate for one and a half hours. The solution was then acidified by hydrochloric acid, evaporated to a thin paste, and extracted exhaustively with ether. When no more material could be recovered in this way, the pasty residue was dried and ground under cold acetone until only inorganic salts remained undissolved.

Pyromellitic Acid (XXIV).

The pale straw-coloured syrup obtained from the ether extract deposited crystals of pyromellitic acid hydrate on rubbing with water. The acid was identified by its melting point (242° for the dihydrate, 273° for the anhydrous acid), by analysis (Found : C = 47·2; H = 2·3. Calc., C = 47·2; H = 2·3 per cent.), and by the melting points of its methyl and ethyl esters (141° and 53° respectively). Methyl pyromellitate was also isolated from the less volatile fractions of the mixture of esters prepared as described on p. 2019.

α-*Ketoglutaric Acid* (XVIII).

This acid may be isolated from the syrupy mixture either as its semicarbazone or phenylhydrazone, but the latter derivative was found to be more suitable for the purpose. It was obtained in the usual manner by means of phenylhydrazine acetate and hydrolysed to α-ketoglutaric acid by means of 30 per cent. sulphuric acid. The product extracted by ether from the acid solution melted at 110—112°, and after crystallising from a mixture of acetone and benzene, at 113°. It was identified as α-ketoglutaric acid by analysis (Found : C = 41·3; H = 4·1. Calc., C = 41·1; H = 4·1 per cent.), by the colour developed with aqueous-alcoholic ferric chloride, and by a mixed-melting-point determination with a genuine specimen (this vol., p. 328).

αβ-*Dihydroxyglutaric Acid* (XV).

The residue which remained when the acetone extract was evaporated consisted very largely of αβ-dihydroxyglutaric acid, a considerable quantity of which crystallised on adding dry ether containing a trace of acetone. The acid melted at 164° and agreed in its properties closely with the description given by Kiliani and Loeffler (*loc. cit.*).

The syrupy mixture of acids recovered from the aqueous solution from which the phenylhydrazone of α-ketoglutaric acid was precipitated yielded a further quantity of αβ-dihydroxyglutaric acid on mixing with successive quantities of dry ether. It was crystallised for analysis from a mixture of methyl acetate and dry ether (Found : C = 36·7; H = 5·1. Calc., C = 36·6; H = 4·9 per cent.).

β-*Hydroxyglutaric Acid* (XIV).

The combined ethereal filtrates from the dihydroxyglutaric acid were evaporated, and the residue digested for several hours with aqueous cupric acetate. The precipitate obtained in this manner was collected, decomposed by aqueous hydrogen sulphide, and the filtrate from the copper sulphide evaporated to dryness. The crystalline residue was finely powdered, exposed in an evacuated desiccator for several days, and then triturated with dry ether, which easily dissolved about half of it, leaving an insoluble portion consisting of a mixture of αβ-dihydroxyglutaric acid and β-hydroxyglutaric acid. These acids were readily separated by crystallising from a mixture of ether and methyl acetate, and the β-hydroxyglutaric acid was identified by analysis (Found : C = 40·7 ; H = 5·3. Calc., C = 40·5 ; H = 5·4 per cent.), and by conversion into glutaconic acid by boiling with alkalis.

Δ^2-cyclo*Propene-1 : 2-dicarboxylic Acid* (IX).

The ethereal washings from the β-hydroxyglutaric acid left on evaporation a cake of crystals consisting chiefly of two acids, Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid and glutaconic acid, which were easily separated by crystallising first from ethyl acetate and ultimately from a mixture of acetone and benzene, the *cyclo*propenedicarboxylic acid being the less soluble. When pure, the *cyclo*propenedicarboxylic acid separated from ethyl acetate in short needles, m. p. 184° without decomposition (Found : C = 46·8 ; H = 3·1 ; *M* (dibasic) = 128. $C_5H_4O_4$ requires C = 46·9 ; H = 3·1 per cent. ; *M* = 128).

The acid seemed to possess little tendency to pass into an anhydride on treatment with acetyl chloride ; however, it instantly reduced cold alkaline permanganate and on reduction by hydriodic acid and phosphorus yielded *trans-cyclo*propane-1 : 2-dicarboxylic acid (below). On boiling with very concentrated methyl-alcoholic potassium hydroxide, it underwent ring-fission, yielding α-ketoglutaric acid (compare p. 2019).

Glutaconic Acid (V).

The more soluble acid accompanying the *cyclo*propenedicarboxylic acid proved to be glutaconic acid, which, after purification, had the correct melting point (135—136°) and properties.

In addition there was obtained from the ultimate residues a syrup, which showed no tendency to crystallise and was too small in quantity to be subjected to any kind of systematic separation. Qualitative tests, however, indicated that glutaconic acid was one of the principal constituents, and therefore, in order to obtain an estimate of the amount present, the crude syrup was digested with acetyl chloride containing 4—5 per cent. of phosphorus trichloride. The crude glutaconic anhydride obtained in this manner was purified by dissolution in cold dilute sodium hydroxide, pouring the solution through a wet filter to remove the suspended oil, and regeneration by adding hydrochloric acid, and was finally converted into the anilic acid by treatment with aniline. The same anilic acid was produced when the crystalline glutaconic acid (above) was treated in a similar manner. It melted at 134° and was evidently the *cis*-isomeride (Found : C = 64·4; H = 5·4. Calc., C = 64·4; H = 5·4 per cent.), since on heating it yielded the *trans*-modification (m. p. 167°), which was identified by comparison with an authentic specimen.

trans-cyclo*Propane*-1 : 2-*dicarboxylic Acid* (XXV).

The aqueous filtrate from the copper salts was worked up for acid products in the usual manner, ether being used as solvent. The excess of acetic acid (derived from the copper acetate) having been removed in a vacuum over solid potassium hydroxide, the syrupy mixture of acids, which had become brown and slightly cloudy owing to partial crystallisation, was esterified with methyl alcohol (3 parts) and sulphuric acid (2 parts), and the esters precipitated by adding water were divided into neutral and acidic fractions by means of ether and sodium carbonate. The acid esters were then re-esterified by the same method and the neutral esters obtained in this way combined with the original neutral product and distilled under reduced pressure. The main portion of the distillate was obtained as a colourless oil, b. p. 125—140°/25 mm., but although it was obviously a mixture, the quantity was insufficient for separation by fractional distillation to be possible. However, from the dark coloured residue in the distilling flask, by treatment with methyl alcohol in the presence of charcoal was obtained a crystalline substance, m. p. 141°, which was identified as methyl pyromellitate by analysis (Found : C = 53·9; H = 4·5. Calc., C = 54·2; H = 4·5 per cent.), and by hydrolysing it to the free acid.

The more volatile esters, b. p. 125—140°/25 mm., were completely hydrolysed by boiling with concentrated (20 per cent.) hydrochloric acid until no more methyl alcohol was liberated. The syrup obtained on evaporation showed little tendency to crystallise, but it gave a red coloration with ferric chloride and on further examination was proved to contain a considerable amount of α-ketoglutaric acid. This was, therefore, removed as completely as possible in the form of its phenylhydrazone and the remaining acids were recovered in the usual manner and freed from adhering acetic acid by evaporation over potassium hydroxide. In the course of a few weeks the product became largely crystalline and was spread on porous plates to drain off the remaining syrup, the last traces of which, along with a small quantity of a crystalline acid (believed to be glutaric acid) were removed by triturating with warm benzene. The examination of the crystalline material was attended with some difficulty, but it was ultimately shown to consist of a mixture of Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid and *trans*-*cyclo*propane-1 : 2-dicarboxylic acid together with at least one other crystalline acid (possibly succinic acid), which could not be definitely identified. All three substances melted in the neighbourhood of 180° and possessed similar solubilities in the usual solvents, and although in preliminary experiments the *cyclo*propene- and *cyclo*propane-dicarboxylic acids were obtained in the pure condition by fractionally crystallising the mixture, it was afterwards found to be a more satisfactory method of separation to precipitate the copper salt of the *cyclo*propenedicarboxylic acid in the presence of 5—10 per cent. of acetone and recover the *cyclo*propanedicarboxylic acid from the filtrate. After purification by crystallising from water, the acid melted at 175° and was identified by direct comparison with a known specimen as *trans*-*cyclo*propane-1 : 2-dicarboxylic acid (Found: C = 46·2; H = 4·8. Calc., C = 46·1; H = 4·6 per cent.).

The yields of the seven acids obtained in this experiment are given in Table I.

(C) *Action of Concentrated Alkalis on αβ-Dibromoglutaric Acid: Formation of αβ-Dihydroxyglutaric Acid, Glutaconic Acid, β-Hydroxyglutaric Acid, Glutaric Acid, α-Ketoglutaric Acid,* cyclo*Propenedicarboxylic Acid,* cis- *and* trans-cyclo*Propanedicarboxylic Acid, Succinic Acid, and Pyromellitic Acid.*

Fifty grams of αβ-dibromoglutaric acid (section A) were added as rapidly as possible to 310 c.c. of a boiling 6*N*-methyl-alcoholic solution of potassium hydroxide. When the violence of the reaction had subsided, the product was heated for thirty minutes, evaporated with water, and then rendered acid by means of concentrated hydrochloric acid. The acid products were extracted by ether and acetone as in the preceding experiment, but in this instance almost the whole of the material passed into the ethereal extract, and the acetone solution yielded only a very small amount of αβ-dihydroxyglutaric acid and some unidentified gummy material.

A considerable quantity of pyromellitic acid crystallised from the ethereal extract on rubbing with a little water, and from the syrupy residue α-ketoglutaric acid, αβ-dihydroxyglutaric acid, β-hydroxyglutaric acid, glutaconic acid, and *cyclo*propenedicarboxylic acid were separated by a series of processes closely similar to that already described up to the stage at which the unresolved residue was esterified with methyl alcohol. By this means the last trace of pyromellitic acid was removed in the form of its relatively non-volatile methyl ester and the remaining acids were freed from the dark coloured impurities which had been formed in the original reaction and had concentrated in the course of the separation. The colourless syrup obtained on hydrolysing the distilled methyl esters by hydrochloric acid was treated, in the first place, with phenylhydrazine acetate, whereby a certain quantity of α-keto-glutaric acid was precipitated as its phenylhydrazone, and then, after removing the excess of phenylhydrazine, with cupric acetate, the solution being concentrated suitably in order to render the precipitation of the copper salt of *cyclo*propenedicarboxylic acid as complete as possible. It was found necessary also to boil the suspension in order to lessen the co-precipitation of other substances. Ultimately, the filtrate was worked up for the acids present, which were obtained, finally, in a concentrated solution in acetic acid (derived from the copper and phenylhydrazine acetates). This solution was boiled for two hours with three times its volume of acetyl chloride and the product evaporated in a vacuum over potassium hydroxide. The partly crystalline residue was dissolved in ether and quickly washed with cold dilute sodium hydrogen carbonate solution. The aqueous layer, on acidification, yielded *trans-cyclo*propane-1 : 2-dicarboxylic acid, but the ethereal solution, on evaporation, left a colourless syrup, which, however, on boiling and finally evaporating with water, gave a wholly crystalline product weighing about 1 gram.

cis-cyclo*Propane*-1 : 2-*dicarboxylic Acid* (XXV).

The crystalline mixture of acids had no definite melting point and was therefore fractionally extracted with dry ether until a sparingly soluble residue, m. p. 136—138°, was obtained. This was crystallised for analysis from a mixture of ethyl acetate and benzene and was identified as *cis-cyclo*propane-1 : 2-dicarboxylic acid (Found: C = 45·9; H = 4·7. Calc., C = 46·1; H = 4·6 per cent.) by comparison with a known specimen of this substance and by conversion into its anhydride (m. p. 59°).

Succinic Acid (XXI).

The acids extracted by boiling ether were recovered by evaporation of the solvent and extracted by means of hot benzene. The insoluble portion melted indefinitely between 165° and 180°, but after one crystallisation from water it melted quite sharply at 184° and was identified as succinic acid by comparison with a genuine specimen (Found : $C = 40{\cdot}3$; $H = 5{\cdot}1$. Calc., $C = 40{\cdot}7$; $H = 5{\cdot}1$ per cent.).

Glutaric Acid (XXVI).

The material extracted by boiling benzene consisted essentially of glutaric acid. In the crude condition, it melted at 88—93°, but after it had been crystallised several times from benzene the melting point rose to 94—95°. Identity was established by a mixed-melting-point determination with a genuine specimen of glutaric acid, and by analysis (Found : $C = 45{\cdot}1$; $H = 6{\cdot}4$. Calc., $C = 45{\cdot}45$; $H = 6{\cdot}1$ per cent.).

The yields are indicated in Table I.

(D) *Action of Dilute Alkalis on Ethyl α-Bromoglutaconate : Formation of α-Ketoglutaric Acid,* cyclo*Propenedicarboxylic Acid,* trans-cyclo*Propanedicarboxylic Acid, and Pyromellitic Acid.*

Twenty-five grams of ethyl α-bromoglutaconate (section A) were boiled for twenty hours with 4·5 equivalents of 2*N*-aqueous sodium carbonate. The homogeneous solution was then acidified, saturated with ammonium sulphate, and extracted repeatedly with ether. The syrupy product deposited only a small amount of crystalline material and was therefore esterified with methyl alcohol as described on p. 2016. The major portion of the methyl esters having been distilled at 120—140°/21 mm., there remained a crystalline residue which was easily purified and identified as methyl pyromellitate. The distillate, on hydrolysis by means of hydrochloric acid, yielded a clear, pale yellow syrup, the principal constituent of which was found to be α-ketoglutaric acid, which was isolated as usual as its phenylhydrazone. The remaining acids were then treated with copper acetate in concentrated aqueous solution in order to precipitate the copper salt of *cyclo*propenedicarboxylic acid and then extracted from the filtrate and treated with acetyl chloride as described on p. 2018, the unchanged acids being separated from the anhydrides by shaking for a few moments with ice-cold dilute sodium hydrogen carbonate. No pure substance was isolated from the anhydrides, but the principal constituent of the unchanged acids proved to be *trans*-*cyclo*propane-1 : 2-dicarboxylic acid, which was readily obtained in the crystalline condition by saturating a concentrated aqueous solution with gaseous hydrogen chloride.

The yields were as stated in Table I.

(E) *Action of Concentrated Alkalis on Ethyl α-Bromoglutaconate: Formation of α-Ketoglutaric Acid,* cyclo*Propenedicarboxylic Acid,* cis- *and* trans-cyclo*Propanedicarboxylic Acid, Succinic Acid, and Pyromellitic Acid.*

Thirty grams of ethyl α-bromoglutaconate (section A) were heated to 100°, and run in a thin stream into 150 c.c. of a boiling 6*N*-methyl-alcoholic solution of potassium hydroxide. The mixture was boiled for thirty minutes and then evaporated several times with water. The residue was acidified with concentrated hydrochloric acid and the organic acids were extracted with pure ether.

The product, after keeping for a few days, deposited a considerable quantity of pyromellitic acid, and on adding a small amount of water a further quantity separated. This was collected and the residual brown syrup esterified with methyl alcohol, and the esters distilled and then rehydrolysed as in the preceding experiments. α-Ketoglutaric acid, *cyclo*propenedicarboxylic acid, and *trans-cyclo*propanedicarboxylic acid were then isolated and obtained in the pure condition exactly as described in the last experiment (section D). The anhydrides corresponding with those which in that instance yielded no recognisable product, in this case gave on rehydration a syrupy mixture of acids, which, in the course of a few months, deposited a relatively considerable quantity of crystals. These were found to consist of approximately equal quantities of *cis-cyclo*propane-1 : 2-dicarboxylic acid and succinic acid, which, after the syrup had been removed by draining on porous porcelain and washing with hot benzene, were easily separated by means of dry ether as described on p. 2018.

The yields of the various acids isolated are given in Table I, column 4.

(F) *Action of Concentrated Alkalis on* Δ^2-cyclo*Propene*-1 : 2-*dicarboxylic Acid* *: *Formation of α-Ketoglutaric Acid.*

The *cyclo*propenedicarboxylic acid was boiled with 6*N*-methyl-alcoholic potassium hydroxide under conditions closely resembling those employed in the experiments already described (sections D and E). The product was worked up for acids in the usual manner and the α-ketoglutaric acid separated in the form of its phenylhydrazone.

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* This experiment might be regarded as evidence against the constitution proposed for this acid, and it must be confessed that the position of the double bond has not yet been satisfactorily established. From the point of view of the present investigation, however, it matters nothing whether the double bond has or has not passed to the Δ^1-position, and the question has therefore been left over for future examination.

We are much indebted to Prof. J. F. Thorpe for his interest in this investigation and to the Chemical Society for a grant which has greatly facilitated it.

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CCXXXII.—*Studies in the Dihydronaphthalene Series. Part II. The* ar-*Dihydro-α-naphthols and their Derivatives.*

By FREDERICK MAURICE ROWE and ESTHER LEVIN.

OUR investigations of the hydrogenation of α-naphthylamine (T., 1918, **113**, 955; *J. Soc. Dyers and Col.*, 1919, **35**, 128; *J. Soc. Chem. Ind.*, 1920, **39**, 241T; T., 1920, **117**, 1574) have shown that the base is converted into *ar*-tetrahydro-α-naphthylamine by the action of sodium and amyl alcohol, but that when the reduction is effected under suitable conditions with sodium and ethyl alcohol in the presence of an inert solvent of high boiling point, such as solvent naphtha or toluene, the intermediate 5 : 8-dihydro-α-naphthylamine only is obtained. The latter is isomerised by the action of sodium ethoxide at a suitable temperature and concentration to 5 : 6(or 7 : 8)-dihydro-α-naphthylamine, a compound which differs from its isomeride in that it may be converted into the tetrahydro-derivative by the action of sodium and ethyl alcohol.

In the case of α-naphthol also the action of sodium and amyl alcohol leads to the formation of the *ar*-tetrahydro-derivative (Bamberger and Bordt, *Ber.*, 1890, **23**, 215; Jacobson and Turnbull, *ibid.*, 1898, **31**, 897). The *ar*-dihydro-α-naphthols corresponding with the two *ar*-dihydro-α-naphthylamines have not been described hitherto, and it appeared of interest, therefore, to prepare and examine these compounds.

In the first place, attempts were made to prepare these compounds by the direct hydrogenation of α-naphthol in a similar manner to that used for the preparation of the dihydro-α-naphthylamines (*loc. cit.*), with the exception that an increased quantity of sodium was employed on account of the acidic nature of the product. The reduction mixture was diluted and distilled in a current of steam to remove the volatile solvent. The residue was then acidified, distilled in a current of steam, and the distillate examined.

(*a*) When α-naphthol, ethyl alcohol, toluene or solvent naphtha, and sodium were employed, the distillate contained a product, melting at 56°, which proved to be a mixture of 5 : 8-dihydro-α-naphthol and 5 : 6(or 7 : 8)-dihydro-α-naphthol, together with a small quantity of unreduced α-naphthol.

(*b*) When α-naphthol, ethyl alcohol, solvent naphtha or toluene, and sodium were employed, and the mixture, after all the sodium had disappeared, was distilled slowly to remove the volatile solvent, and then heated for one hour at 125°, the product proved to be a mixture of 5 : 6(or 7 : 8)-dihydro-α-naphthol with some unreduced α-naphthol. Separation of this mixture was at first effected by means of fractional distillation in a current of steam, as the hydrogenated naphthol is more volatile than α-naphthol, but later, when it was found that the hydrogenated naphthol did not form a picrate, it proved more satisfactory to remove the α-naphthol from the mixture by conversion into the picrate. 5 : 6(or 7 : 8)-Dihydro-α-naphthol forms colourless plates or needles, melting at 71°.

As a result of these experiments it appears that, in the case of α-naphthol, it is more difficult to determine conditions suitable for the preparation of the 5 : 8-dihydro-derivative than is the case with α-naphthylamine, for, although the conditions were varied, in all cases where hydrogenation occurred, the product was a mixture of the two dihydro-α-naphthols, owing to the fact that some of the 5 : 8-dihydro-derivative was isomerised during the reaction. This is, however, not surprising, for in view of the increased concentration of alkali used in these experiments, it is probable that conditions which are favourable for the hydrogenation of α-naphthol to its 5 : 8-dihydro-derivative are equally favourable for the isomerisation of this compound to the 5 : 6(or 7 : 8)-dihydro-α-naphthol.

Therefore, whilst the method (*b*) outlined above was suitable for the preparation of 5 : 6(or 7 : 8)-dihydro-α-naphthol, the method (*a*) was unsuitable for the preparation of the 5 : 8-derivative, as we were unable to separate the mixture of the two dihydro-compounds formed.

Attention was next directed to the preparation of the dihydro-α-naphthols from the corresponding amines by diazotisation and boiling the diazonium compound.

It is noteworthy that whilst this method gives good results in the case of the preparation of *ar*-tetrahydro-α-naphthol from *ar*-tetrahydro-α-naphthylamine (Bamberger and Althausse, *Ber.*, 1888, 21, 1892), the yields of the dihydro-α-naphthols from the corresponding dihydro-amines are low, and these compounds are always formed together with a considerable proportion of naphthalene.

5 : 8-Dihydro-α-naphthol forms colourless plates or needles, melting at 75°, with a pronounced phenolic odour, whilst 5 : 6-(or 7 : 8)-dihydro-α-naphthol also forms colourless plates or needles, melting at 71°, identical with the product previously described and obtained by the direct hydrogenation of α-naphthol and isomerisation of the intermediate 5 : 8-dihydro-α-naphthol.

The following table indicates the behaviour of aqueous solutions of α-naphthol, 5 : 8-dihydro-α-naphthol, 5 : 6(or 7 : 8)-dihydro-α-naphthol, and *ar*-tetrahydro-α-naphthol on the addition of ferric chloride and calcium hypochlorite respectively :

	α-Naphthol.	5 : 8-Dihydro-α-naphthol.	5 : 6(or 7 : 8)-Dihydro-α-naphthol.	*ar*-Tetrahydro-α-naphthol.
Ferric chloride.	Violet colour and precipitate.	A more reddish-violet colour and precipitate which develops more slowly than is the case with α-naphthol.	Brown colour and precipitate.	Yellow colour and precipitate.
Calcium hypochlorite.	,, ,,	A much redder colour and precipitate than with α-naphthol.	,, ,,	Faint white precipitate.

An important difference in the properties of 5 : 8-dihydro-α-naphthol and 5 : 6(or 7 : 8)-dihydro-α-naphthol is shown by their behaviour on treatment with sodium and ethyl alcohol, for the 5 : 8-isomeride remains unchanged, whilst the 5 : 6(or 7 : 8)-isomeride is converted into *ar*-tetrahydro-α-naphthol.

It is clear, therefore, that the course of the reaction in the conversion of α-naphthol into *ar*-tetrahydro-α-naphthol by means of sodium and an alcohol is completely analogous to the course of the reactions in the hydrogenation of naphthalene and α-naphthylamine under similar conditions, and the intermediate dihydro-derivatives in each case exhibit a similar behaviour when treated with sodium and ethyl alcohol.

The behaviour of the two dihydro-α-naphthols when sulphonated and nitrated under conditions similar to those employed for *ar*-tetrahydro-α-naphthol (*loc. cit.*) was next examined. When the dihydro-α-naphthols are treated with twice their weight of concentrated sulphuric acid for two days at the ordinary temperature, they are converted, for the greater part, into water-soluble products, although sulphonation is accompanied to a certain extent by resinification. The crude sodium salts of the sulphonic acids could be isolated from the sulphonation mixtures in the usual manner. The sulphonic acids are readily hydrolysed by dilute acids with regeneration of the dihydro-α-naphthols. From analogy to the monosulphonic acid of *ar*-tetrahydro-α-naphthol it was to be expected that the sulphonic group would enter the *para*-position with respect to the hydroxyl group in the dihydro-α-naphthols, and that this was the case is obvious from the behaviour of the sulphonic acids on nitration.

5 : 8-Dihydro-α-naphthol-4-sulphonic acid and 5 : 6(or 7 : 8)-dihydro-α-naphthol-4-sulphonic acid possess similar properties to *ar*-tetrahydro-α-naphthol-4-sulphonic acid, and, for example, in alkaline solution do not combine with diazonium compounds to form azo-dyes.

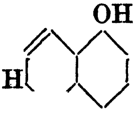
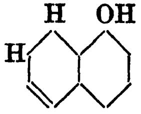
For the nitration experiments it is unnecessary to isolate the sulphonic acids, but the diluted sulphonation mixtures were nitrated directly, and 2-nitro-5 : 8-dihydro-α-naphthol, yellow needles, melting at 98°, volatile with steam, 2-nitro-5 : 6(or 7 : 8)-dihydro-α-naphthol, yellow needles, melting at 55°, volatile with steam, and 2 : 4-dinitro-5 : 8-dihydro-α-naphthol, yellow, prismatic needles, melting at 127°, were obtained.

Both dihydro-α-naphthols exhibited behaviour similar to that of *ar*-tetrahydro-α-naphthol when treated with nitrous acid, and yielded 4-nitro-5 : 8-dihydro-α-naphthol, brown needles, melting at 161°, and 4-nitro-5 : 6(or 7 : 8)-dihydro-α-naphthol, yellow needles, melting at 162°, respectively.

All attempts to obtain 2 : 4-dinitro-5 : 6(or 7 : 8)-dihydro-α-naphthol either by nitration of the dihydronaphtholsulphonic acid with two molecules of nitric acid or by the further nitration of 4-nitro-5 : 6(or 7 : 8)-dihydro-α-naphthol with nitric acid resulted in complete resinification of the compound.

It should be noted that whereas the nitration of *ar*-tetrahydro-α-naphthol under the conditions described results in almost theoretical yields of the nitro-derivatives in all cases, the dihydro-α-naphthols are, on nitration, more readily oxidised under the existing conditions, and give extremely low yields of the nitro-derivatives. This behaviour is not surprising, however, in view of the unsaturated character of the hydrogenated ring in the dihydro-α-naphthols.

EXPERIMENTAL.

5 : 6(or 7 : 8)-*Dihydro-α-naphthol*,  or  .

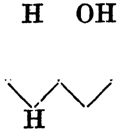
(1) A mixture of 400 c.c. of dry toluene or solvent naphtha (b. p. 139°) and 70 grams of sodium was boiled in a flask fitted with a reflux condenser, and a solution of 30 grams of α-naphthol in rather more ethyl alcohol than is necessary to dissolve the sodium was added drop by drop through the condenser. Boiling was continued until all the sodium had disappeared, and the mixture was then distilled until the internal temperature rose to 125°, at which temperature heating was continued for one hour. The mixture was poured into water and distilled in a current of steam to remove the remainder of the toluene. The residue was acidified with hydrochloric acid and distilled in a current of steam. The distillate was saturated with sodium chloride, as the dihydronaphthol is appreciably soluble in water, and the crystalline product separated. Any unaltered α-naphthol was removed by conversion into its picrate.

5 : 6(or 7 : 8)-*Dihydro-α-naphthol* forms colourless, silky needles or plates, melting at 71° (corr.) (Found: C = 82·19; H = 6·79. $C_{10}H_{10}O$ requires C = 82·19; H = 6·85 per cent.).

(2) Fifteen grams of 5 : 6(or 7 : 8)-dihydro-α-naphthylamine were stirred into 25 grams of sulphuric acid diluted with 100 c.c. of water, and the crystalline paste, cooled to 2°, was diazotised with a solution of 7·2 grams of sodium nitrite in 100 c.c. of water. The yellowish-red solution was kept for half an hour, warmed gently until the evolution of nitrogen ceased, distilled in a current of steam, and the distillate saturated with sodium chloride. The product, a mixture of 5 : 6(or 7 : 8)-dihydro-α-naphthol and naphthalene, was extracted with sodium hydroxide, the extract was acidified, and the regenerated dihydronaphthol purified by distillation in a current of steam. The product was identical with that obtained by the direct hydrogenation of α-naphthol (Found: C = 81·99; H = 6·66 per cent.).

ar-Tetrahydro-α-naphthol is readily obtained from 5 : 6 (or 7 : 8)-dihydro-α-naphthol by the gradual addition of 30 grams of sodium to a boiling solution of 10 grams of this dihydro-α-naphthol in 400 c.c. of dry ethyl alcohol. The *ar*-tetrahydro-α-naphthol was isolated in the usual manner.

5 : 8-*Dihydro*-α-*naphthol*,



This compound was prepared from 5 : 8-dihydro-α-naphthylamine in a similar manner to that described for the preceding compound. 5 : 8-Dihydro-α-naphthol forms colourless plates or needles, melting at 75° (Found: C = 81·99; H = 6·92. $C_{10}H_{10}O$ requires C = 82·19; H = 6·85 per cent.). When heated with a solution of sodium ethoxide, it is converted into 5 : 6 (or 7 : 8)-dihydro-α-naphthol.

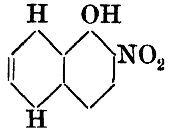
Sulphonation of 5 : 8-*Dihydro*-α-*naphthol.*

Ten grams of finely powdered 5 : 8-dihydro-α-naphthol having been completely dissolved in 20 grams of cold concentrated sulphuric acid, the solution was kept for two days at the ordinary temperature, and the mixture was then diluted with water and filtered from a trace of unsulphonated 5 : 8-dihydro-α-naphthol. The filtrate was neutralised with milk of lime, and the calcium salt, after removal of calcium sulphate, was converted into the sodium salt and evaporated to dryness. The sodium salt could not be obtained in a pure condition for analysis owing to the presence of resinous matter. It is very readily soluble in water, and the sulphonic group is readily hydrolysed by boiling with dilute acids, 5 : 8-dihydro-α-naphthol being regenerated. 5 : 8-Dihydro-α-naphthol-4-sulphonic acid, in neutral or alkaline solution, does not couple with diazonium salts to form azo-compounds.

Sulphonation of 5 : 6(or 7 : 8)-*Dihydro*-α-*naphthol.*

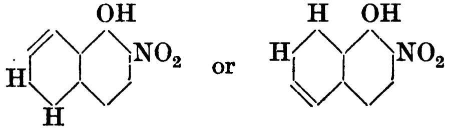
This sulphonation was effected in a similar manner to that described for the preceding compound. The product, which could not be obtained in a sufficiently pure condition for analysis, possesses similar properties to those of its isomeride.

2-*Nitro*-5 : 8-*dihydro*-α-*naphthol*,



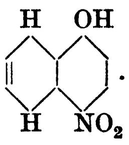
Two grams of 5 : 8-dihydro-α-naphthol were dissolved in 4 grams of cold concentrated sulphuric acid. The solution was allowed to remain for two days, diluted with 6·5 c.c. of water, cooled in ice and nitrated with 0·9 c.c. of nitric acid (*d* 1·4; 1 mol.) diluted with 2 c.c. of water. The nitrosulphonic acid did not separate from the mixture as did the corresponding compound during the nitration of *ar*-tetrahydro-α-naphthol-4-sulphonic acid under the same conditions. The nitrosulphonic acid, therefore, was not isolated in this case, but the nitration mixture was boiled with dilute sulphuric acid (1 : 1) in order to hydrolyse the sulphonic group, and then distilled in a current of steam. 2-*Nitro*-5 : 8-*dihydro-α-naphthol* forms yellow needles, melting at 98°. It is readily volatile with steam and possesses a sweet, pleasant odour. It dissolves in sodium hydroxide solution with an orange coloration, forms an orange-red sodium salt, and couples with diazonium compounds forming azo-dyes (Found: C = 62·71; H = 4·80; N = 7·13. $C_{10}H_9O_3N$ requires C = 62·82; H = 4·71; N = 7·33 per cent.).

2-*Nitro*-5 : 6(or 7 : 8)-*dihydro-α-naphthol*,



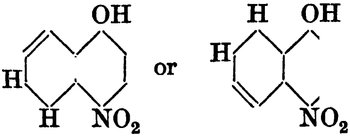
This compound was prepared in the same manner as that described for the preceding compound. It forms yellow needles, melting at 55°, and possesses similar properties to those of 2-nitro-5 : 8-dihydro-α-naphthol (Found: C = 62·71; H = 4·84; N = 7·50. $C_{10}H_9O_3N$ requires C = 62·82; H = 4·71; N = 7·33 per cent.).

4-*Nitro*-5 : 8-*dihydro-α-naphthol*,



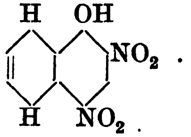
Five grams of 5 : 8-dihydro-α-naphthol were dissolved in sodium hydroxide, the solution being diluted with water to 150 c.c. To this, an aqueous solution of 3·6 grams of sodium nitrite (2 mols.) was added together with 100 grams of ice. Fifty c.c. of 10 per cent. sulphuric acid contained in a dropping funnel, the end of which dipped below the surface of the liquid, were then slowly run into the mixture with constant agitation. The sticky, yellowish-white precipitate was collected and washed with cold water. The major portion dissolved in sodium carbonate solution, and was filtered from a quantity of a tarry residue. From the filtrate, the product was precipitated by dilute acetic acid. 4-*Nitro*-5 : 8-*dihydro-α-naphthol* crystallises from dilute alcohol in brown needles, melting at 161° (with decomp.). It is not volatile with steam. It dissolves in sodium hydroxide solution with a yellowish-brown coloration, and on addition of excess of alkali, the sodium salt crystallises in brown needles. 4-Nitro-5 : 8-dihydro-α-naphthol does not couple with diazonium compounds (Found : C = 62·79; H = 4·78; N = 7·15. $C_{10}H_9O_3N$ requires C = 62·82; H = 4·71; N = 7·33 per cent.).

4-*Nitro*-5 : 6(or 7 : 8)-*dihydro-α-naphthol*,



This compound was prepared in the same manner as that described for the preceding compound. It crystallises from dilute alcohol in yellow needles, melting at 162° (with decomp.). Its properties are similar to those of 4-nitro-5 : 8-dihydro-α-naphthol (Found : C = 62·99; H = 4·75; N = 7·15. $C_{10}H_9O_3N$ requires C = 62·82; H = 4·71; N = 7·33 per cent.).

2 : 4-*Dinitro*-5 : 8-*dihydro-α-naphthol*,



Four grams of 5 : 8-dihydro-α-naphthol were dissolved in 8 grams of cold concentrated sulphuric acid, the solution was allowed to remain for two days, and diluted with 10 c.c. of water. The clear liquid was cooled in ice, and nitrated with 4·7 c.c. of nitric acid (*d* 1·4; 2·5 mols.) diluted with 5·5 c.c. of water. After all the nitric acid had been added, the mixture was allowed to remain at the ordinary temperature for some time. It was then warmed on the water-bath at 50° until a semi-crystalline product, insoluble in water, had separated. A quantity of resinous impurity was removed from the product by careful washing with cold toluene.

2 : 4-*Dinitro*-5 : 8-*dihydro-α-naphthol* crystallises from ether in long, yellow, prismatic needles, melting at 127°. It dissolves in sodium hydroxide solution with an orange-brown coloration, and the sodium salt crystallises from the solution in orange needles

(Found: C = 50·75; H = 3·36; N = 11·99. $C_{10}H_8O_5N_2$ requires C = 50·85; H = 3·39; N = 11·87 per cent.).

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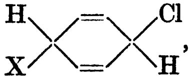
CCXXXIII.—*Researches on Sulphuryl Chloride. Part I. Influence of Catalysts: a Convenient Method of Chlorinating Benzene.*

By OSWALD SILBERRAD.

THE present investigation was instituted with the two-fold object of devising a convenient method of chlorinating the less reactive benzenoid hydrocarbons with sulphuryl chloride and also of throwing additional light on chlorination generally. Heretofore sulphuryl chloride has been little used for the chlorination of such compounds owing to the difficulty with which it reacts; thus Dubois (*Zeitsch. Chem.* von Beilstein u. Fritz Hubner, 1866, **2**, 705) found it necessary to heat it at 150° in sealed tubes with benzene in order to effect chlorination, whilst Töhl and Eberhard (*Ber.*, 1893, **26**, 2941) found 160—170° necessary. The present investigation has, however, shown that in the presence of suitable catalysts this hydrocarbon may be chlorinated in a few minutes at the ordinary temperature (for details see below, experiments Nos. 6, 7, 8, and 9), and, further, that in all cases where rapid chlorination is induced the reaction is accompanied by the formation of intensely coloured intermediate compounds probably of the type 

, thus giving interesting evidence respecting the additive theory of chlorination (compare Kekulé, *Annalen*, 1858, **106**, 129; Michael, *J. pr. Chem.*, 1883, [ii], **37**, 486; van't Hoff, " Ansichten über Organische Chemie," I, 225, 244; Schmidlin and Lange, *Ber.*, 1910, **43**, 2806; 1912, **45**, 1899).

Broadly speaking, the catalysts investigated divide themselves into two groups, namely, those dependent on the liberation of free chlorine due to the dissociation of the sulphuryl chloride, and those the action of which involves the formation of some intensely coloured intermediate compound, to which there is every reason to assign a structure of the type indicated above (compare H. E. Armstrong, P., 1888, **4**, 27).

Of the first group of catalysts investigated, iodine induces chlorination to the extent of 17 per cent. on boiling for eight hours;* thionyl chloride 24 per cent. in the same time; sulphur or sulphur chloride 37 per cent., and ferric chloride 53 per cent.† The reason for this wide difference in velocity becomes evident on considering the properties of an admixture of the reacting substances with sulphuryl chloride. Iodine acts as a simple carrier dependent on the dissociation of sulphuryl chloride for the formation of iodine trichloride (compare Ruff, *Ber.*, 1901, **34**, 1749). Thionyl chloride has been shown to behave as a mixture of sulphur dioxide and sulphur tetrachloride under certain conditions (Prinz, *Annalen*, 1884, **223**, 355); it therefore appears probable that the latter compound is the active chlorinating agent in this case and also when sulphur or sulphur chloride is present, both of which are converted into higher chlorides by excess of sulphuryl chloride (Ruff, *loc. cit.*, p. 1750). Ferric chloride acts, not only as a carrier, but also, as is often the case with this reagent, in a manner similar to aluminium chloride by inducing dissociation of the sulphuryl chloride (compare Ruff, *Ber.*, 1902, **35**, 4453; *Chem. Zeit.*, 1906, **30**, 1225; Roland, *Chem. Zeit.*, 1906, **30**, 1173).

The second series of catalysts differs materially from those considered above in that their action is accompanied by the production of much more intensely coloured substances, and also in that they induce incomparably more vigorous chlorination. They consist of aluminium chloride together with some sulphur compound, the simplest case being when sulphuryl chloride itself acts in this capacity also. In this connexion it should be observed that the action of aluminium chloride on a mixture of sulphuryl chloride and benzene under conditions conducive to the Friedel and Crafts reaction has already been investigated by Töhl and Eberhard (*loc. cit.*), who, working under these conditions, obtained chiefly benzenesulphonyl chloride together with a smaller quantity of diphenylsulphone and about 4½ per cent. of chlorobenzene; this work was subsequently confirmed and elaborated by Böeseken (*Rec. trav. chim.*, 1911, **30**, 381), who, working under conditions even more suited to the Friedel and Crafts reaction, succeeded in isolating benzenesulphinic acid as well as the above compounds.

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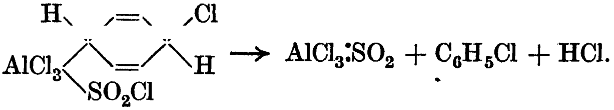
* Töhl and Eberhard (*Ber.*, 1893, **26**, 2941) obtained chlorobenzene by heating a mixture of benzene with sulphuryl chloride and iodine at 150° in sealed tubes. D.R.-P. 269249, which relates to the chlorination of 3-methylanthraquinone by means of sulphuryl chloride in the presence of nitrobenzene, also claims the use of iodine as a catalyst.

† Quite recently Durrans made use of ferric chloride in effecting the chlorination of triphenyl phosphate, which is not attacked by sulphuryl chloride alone (private communication).

When, however, sulphuryl chloride is rapidly run into a boiling mixture of benzene and aluminium chloride, chlorination occurs almost to the exclusion of all other reactions, the yield being about 90 per cent. of the theoretical, whilst the reacting mass, which at first assumes a vandyke-brown hue, subsequently turns to an intense violet-brown. This remarkable reaction appears to be traceable to the tendency of aluminium chloride to form a double compound both with the hydrocarbon and also with the sulphuryl chloride, the probable constitution and decomposition of which may well be indicated by the following equation:



Additional probability is lent to this suggestion by the fact that the reaction becomes vigorous at the same temperature at which Ruff observed the compound $AlCl_3{:}SO_2$ to break up with regeneration of the aluminium chloride (*Ber.*, 1902, **35**, 4453). The addition of thionyl chloride to the above mixture materially reduces the temperature at which the action takes place, whilst the presence of sulphur or sulphur chloride brings about vigorous chlorination in the cold, the end product being in this case intensely indigo-blue. The constitution of this coloured compound is probably similar to that suggested above; the precise nature is, however, still under investigation.

EXPERIMENTAL.

In order to avoid repetition, the method adopted in investigating the influence of the various catalysts examined on the chlorination of benzene with sulphuryl chloride is here briefly set forth in general terms: The required hydrocarbon (156 grams of benzene; 2 mols.), together with the catalyst in question, was placed in a flask submerged in a water-bath and provided with an efficient reflux condenser, the upper portion of which was loosely packed with asbestos and connected through a trap with a flask containing 10 litres of water in order to absorb the sulphur dioxide and hydrochloric acid gas which are copiously evolved during the reaction. A 5 per cent. excess of sulphuryl chloride (284 grams) was then run in, the water-bath being maintained at such a temperature that a vigorous reaction occurred, or, in the event of no vigorous action taking place, at the boiling point of the mixture. The reaction was allowed to proceed for eight hours, except in such cases as it was complete in a shorter time. The product was then freed from any remaining sulphuryl chloride by agitation with water, steam-distilled, and the relative degree of chlorination ascertained by determining the density of the distillate; from the figure thus obtained the composition was calculated on the assumption that the product consisted of a mixture of chlorobenzene together with unaltered benzene, or dichlorobenzene, as the case might be: the exact nature of the constituents was subsequently established by submitting the steam-distillate to systematic fractionation and identifying the products isolated in the usual manner. Operating in this way, the influence of the following catalysts was examined with the following results:

Experiment No. 1. *Catalyst Iodine.*

Reaction.—On mixing the ingredients (benzene, 156 grams; sulphuryl chloride, 284 grams; iodine, 5 grams), no reaction occurs; on boiling, the red coloration due to iodine slowly disappears as the iodine is converted into the trichloride, and the liquid assumes a ruddy brown colour. During the whole experiment a slow, steady stream of sulphur dioxide and hydrochloric acid gas is evolved: the reaction is evidently not completed by boiling for the duration of the experiment, namely, eight hours.

Yield.—On steam distillation an oil (148 grams) having $d^{21°}$ 0·927 was obtained; this corresponds with a yield of 38 grams of chlorobenzene, from which it would appear that iodine induces the chlorination of 16·8 per cent. of the benzene in eight hours under the above conditions.

Identification.—10·5 Grams of pure chlorobenzene were isolated by fractionation (Found: Cl = 31·22. Calc., Cl = 31·50 per cent.).

Experiment No. 2. *Catalyst Thionyl Chloride.*

Reaction.—On mixing the ingredients (benzene, 156 grams; thionyl chloride, 5 grams; sulphuryl chloride, 284 grams), no reaction occurs; on heating, the liquid, which at first is colourless, rapidly assumes a pink shade, and a slow stream of sulphur dioxide and hydrochloric acid gas is evolved; eight hours' boiling fails to complete the reaction.

Yield.—On steam distillation, an oil (163 grams) having $d^{21°}$ 0·945 was obtained; this corresponds with a yield of 54·5 grams of chlorobenzene, hence thionyl chloride induces chlorination to the extent of 24 per cent. of the benzene in eight hours under the above conditions.

Identification.—Thirty-six grams of pure chlorobenzene were isolated on fractionation (Found: Cl = 31·11 per cent.).

Experiment No. 3. Catalyst Sulphur.

Reaction.—On dissolving the sulphur (5 grams) in the benzene (156 grams) and adding the sulphuryl chloride (284 grams), no action occurred in the cold; on boiling, a slow stream of sulphur dioxide and hydrochloric acid gas was evolved and the liquid, which in the first instance possessed a pale lemon tint, gradually assumed a decided amber yellow. The reaction was not complete at the expiration of eight hours' boiling.

Yield.—On steam distillation, an oil (166 grams) having $d^{21°}$ 0·978 was obtained. This corresponds with a yield of 83 grams of chlorobenzene, hence sulphur under the above conditions induces chlorination to the extent of 37 per cent. of the benzene used in eight hours.

Identification.—Fifty-one grams of pure chlorobenzene were isolated by fractionation (Found: Cl = 31·13 per cent.).

Experiment No. 4. Catalyst Sulphur Chloride.

Reaction.—On mixing the ingredients together (benzene, 156 grams; sulphuryl chloride, 284 grams; sulphur chloride, 5 grams), there was no action in the cold; on boiling, a slow, steady evolution of sulphur dioxide and hydrochloric acid gas occurred, and the liquid, which at first was pale lemon-yellow, developed a clear amber colour. The reaction was not complete after eight hours boiling.

Yield.—On steam distillation, an oil (160 grams) having $d^{21°}$ 0·985 was obtained. This corresponds with a yield of 84 grams of chlorobenzene, hence sulphur chloride under the above conditions induces chlorination to the extent of 37 per cent. of the benzene used in eight hours.

Identification.—Fifty-four grams of pure chlorobenzene were isolated by fractionation (Found: Cl = 31·28 per cent.).

Experiment No. 5. Catalyst Ferric Chloride.

Reaction.—On mixing the ingredients (benzene, 156 grams; sulphuryl chloride, 284 grams; anhydrous ferric chloride, 5 grams), no reaction occurred in the cold; on boiling, a stream of sulphur dioxide and hydrochloric acid gas was evolved; the reaction was evidently not completed at the expiration of eight hours at the boiling point of the mixture. During the operation the product turned through amber yellow to a ruddy brown.

Yield.—On steam distillation, an oil (174 grams) having $d^{21°}$

1·024 was obtained; this corresponds with a yield of 119 grams of chlorobenzene, from which it would appear that ferric chloride induces chlorination to the extent of 53 per cent. of the benzene in eight hours under the above conditions.

Identification.—Ninety grams of pure chlorobenzene were isolated on fractionation (Found : Cl = 31·36 per cent.), also 2 grams of *p*-dichlorobenzene, m. p. 53°.

Experiment No. 6. *Catalyst Aluminium Chloride* (*Anhydrous*).

Ingredients.—Benzene, 156 grams; sulphuryl chloride, 284 grams; anhydrous aluminium chloride, 5 grams.

Reaction.—The benzene and aluminium chloride were mixed, a few c.c. of sulphuryl chloride added, and the temperature of the bath raised until the slight reaction which started in the cold became vigorous—this occurred at 60—70°, at which temperature the remainder of the sulphuryl chloride was rapidly added. During the operation, which occupied forty-five minutes and was accompanied by the copious evolution of sulphur dioxide and hydrochloric acid gas, the mixture, which on the first addition of sulphuryl chloride assumed a deep vandyke-brown colour, passed through black to intense violet-brown, the precise shade of which varied considerably when benzene containing thiophen or traces of toluene was used.

Yield.—On steam distillation, an oil (200 grams) having $d^{21°}$ 1·105 was obtained; this corresponds with 199 grams of chlorobenzene, or a yield amounting to 89 per cent. of the theoretical.

Identification.—One hundred and eighty-one grams of pure chlorobenzene were isolated on fractionation (Found : Cl = 31·48 per cent.).

Experiment No. 7. *Catalyst Aluminium Chloride and Thionyl Chloride.*

Ingredients.—Benzene, 156 grams; sulphuryl chloride, 284 grams; aluminium chloride, 5 grams; thionyl chloride, 1 gram.

Reaction.—On adding the thionyl chloride to the benzene and aluminium chloride, which had been previously mixed, the liquid turned dark brown and, on adding the sulphuryl chloride to this mixture, a fairly vigorous reaction set in at the ordinary temperature; the operation was completed by warming at 80° and occupied in all forty-five minutes, the final product being intensely violet-brown. The reaction was considerably more vigorous than when aluminium chloride alone formed the catalyst (No. 6).

Yield.—On steam distillation, an oil (200 grams) having $d^{21°}$

1·121 was obtained: this corresponds with 186 grams of chlorobenzene and 14 grams of dichlorobenzene, from which it would appear that 83 per cent. of the available chlorine had passed into the hydrocarbon.

Identification.—One hundred and fifty-two grams of pure chlorobenzene were isolated on fractionation (Found: Cl = 31·62 per cent.), also 5 grams of *p*-dichlorobenzene, m. p. 53°.

Experiment No. 8. *Catalyst Aluminium Chloride and Sulphur.*

Ingredients.—Benzene, 156 grams; sulphuryl chloride, 284 grams; aluminium chloride, 5 grams; sulphur, 1 gram.

Reaction.—The sulphur was dissolved in the benzene, the aluminium chloride added, and a few c.c. of sulphuryl chloride run in; the temperature of the bath was then raised until the slight reaction which started in the cold became vigorous, which occurred at about 40°, at which temperature the remainder of the sulphuryl chloride was added. The whole operation occupied fifty-five minutes, during which time the liquid assumed first a vandyke-brown colour, then black, and finally pure indigo-blue. In carrying out this operation, it is important that the sulphur be completely in solution before starting, as otherwise the reaction may be delayed in starting and subsequently become uncontrollable.

Yield.—On steam distillation, an oil (187 grams) having $d^{21°}$ 1·156 was obtained; this corresponds with 143 grams of chlorobenzene and 44 grams of dichlorobenzene, from which it would appear that 89 per cent. of the available chlorine has passed into the hydrocarbon.

Identification.—One hundred and twenty grams of pure chlorobenzene were obtained by fractionation (Found: Cl = 31·55 per cent.), also 15 grams of *p*-dichlorobenzene, m. p. 53°.

Experiment No. 9. *Catalyst Aluminium Chloride and Sulphur Chloride.*

Ingredients.—Benzene, 156 grams; sulphuryl chloride, 284 grams; aluminium chloride, 5 grams; sulphur chloride, 1 gram.

Reaction.—On adding the sulphur chloride to the mixture of benzene and aluminium chloride, the liquid turned deep green, which changed to bluish-black as soon as the sulphuryl chloride was added, and so vigorous a reaction set in that the temperature of the surrounding bath, which at the beginning of the experiment stood at 20°, rose 10° during the addition of this compound. The reaction was complete in thirty minutes, the product being intensely blue.

Yield.—On steam distillation, an oil (183 grams) having $d^{21°}$ 1·137 was obtained; this corresponds with a yield of 156 grams of chlorobenzene and 27 grams of dichlorobenzene, from which it would appear that 87 per cent. of the available chlorine has passed into the hydrocarbon.

Identification.—One hundred and thirty grams of pure chlorobenzene were isolated by fractionation (Found: Cl= 31·82 per cent.), also 7 grams of *p*-dichlorobenzene, m. p. 53°.

The author's thanks are due to Messrs. A. Boake, Roberts and Co., Ltd., for supplying the sulphuryl chloride required for this investigation.

THE SILBERRAD RESEARCH LABORATORIES,
BUCKHURST HILL, ESSEX. [*Received, November 5th*, 1921.]

CCXXXIV.—*The Adsorption of Thorium-*B *and Thorium-*C *by Ferric Hydroxide.*

By JOHN ARNOLD CRANSTON and ROBERT ALEXANDER BURNETT.

IT has been found by McCoy and Viol (*Phil. Mag.*, 1913, [vi], **25**, 340) that "ferric iron precipitated by fumaric acid from a boiling, nearly neutral solution of thorium-*B* and thorium-*C* carries down all the -*C* and only a small part of the -*B*." By redissolving the precipitated iron with the radioactive matter adsorbed and repeating the process, it is claimed that thorium-*C* can be obtained in which no thorium-*B* can be detected after the decay of the former. This process is recommended by these authors as a method of separating thorium-*C* in a state of radioactive purity.

In view of the number of recent publications on the determination of acidity in weakly acid solutions, and the marked influence of the hydrogen ion on many reactions, it seemed desirable to investigate more closely this adsorption effect. Careful measurements have been made of the acidity of the solutions used, and of the ratio in which thorium-*B* and thorium-*C* were adsorbed, with a view to determine whether any connexion exists between these two factors.

The ratio of thorium-*B* to thorium-*C* is readily determined from the form of the decay curve. Pure thorium-*C* decays with the period of half change 1 hour, giving out α-rays; pure thorium-*B* shows no initial α-activity, but develops an activity that rises to a maximum in 3⅔ hours and then decays with the period of half change 10·6 hours. In a mixture of thorium-*B* and thorium-*C*, the amount of -*C* is proportional to the initial activity, whilst the amount of -*B* originally present can be calculated from the residual activity after the decay of the original thorium-*C*, that is, after about six hours.

In the following experiments the activities were measured throughout in the α-ray electroscope and the ratio of thorium-*B* to -*C* calculated from the form of the decay curve. The acid used was hydrochloric, a stock solution being diluted to the various strengths required. With a dilute solution of ferric chloride, about 2 grams per litre, it was found that in acid solution hydrolysis took place with precipitation of ferric hydroxide under the following conditions :

Volume of hydrochloric acid used = 15 to 25 c.c.
Maximum normality of the acid = $N/20$.
Volume of $N/10$-fumaric acid solution, or sodium fumarate = 3 c.c.
Volume of standard ferric chloride = 3 c.c.

When the whole was raised to boiling, hydrolysis was complete in a few minutes.

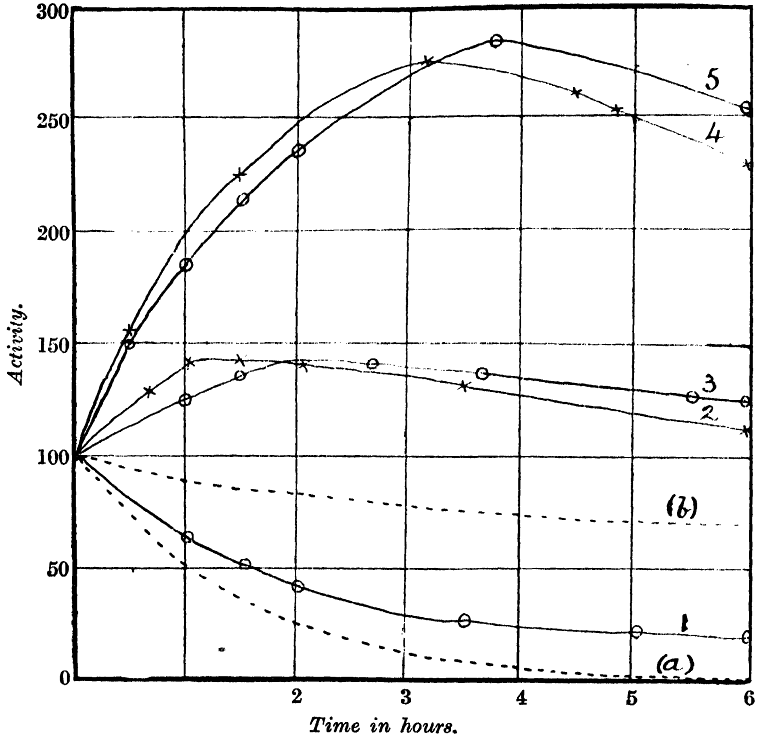
In the first series of experiments the active deposit of thorium-*B* and thorium-*C*, obtained in the usual way by exposing a negatively charged plate to thorium hydroxide, was dissolved in 15 c.c. of hydrochloric acid each time, the strength of the acid being varied. Solutions of sodium fumarate and ferric chloride were added in the quantities stated above, and the whole boiled to precipitate the iron. The precipitate was washed, quickly dried, and the activity on the filter-paper determined for several hours. The actual decay curves obtained are shown in Fig. 1 along with the dotted curves (*a*) and (*b*), which are the theoretical curves for pure thorium-*C* and for the equilibrium mixture respectively. The scale of activities is so chosen that the initial activity in each case is 100. The results are tabulated below in a somewhat different form, the acidity being expressed as normality of hydrochloric acid used and the ratio given as atoms of thorium-*B* per atom of thorium-*C*. In the original active deposit, where the two members were present in radioactive equilibrium, this ratio had the value 10·6.

Normality of acid...............	0·029	0·014	0·007	0·004	0·003
Atomic ratio, Th-*B*/Th-*C*......	3·1	17·7	18·3	33·7	37·7

From these figures it is apparent that, in the most strongly acid solution, thorium-*C* is adsorbed in considerable excess of the equilibrium ratio, and the decay curve (No. 1) is not very different from that of pure thorium-*C*. But as the acidity is decreased the relative amount of thorium-*B* increases, until from the most weakly acid solution thorium-*B* is adsorbed in large excess, and the decay curve shows a maximum activity characteristic of thorium-*B*.

It was recognised, however, that in these experiments the normality of the acid as given represents the total hydrochloric acid added, but does not represent the concentration of hydrogen ion after the precipitation. Part of the hydrochloric acid would act on the sodium fumarate to liberate free fumaric acid which, as an organic dibasic acid, would be only slightly ionised. The actual concentration of hydrogen ion would thus be lower than is indicated by the normality. Another and opposing factor is the hydrochloric acid liberated in the solution by the hydrolysis of the ferric chloride. The precipitate of iron contained about 6—10 mg. of ferric oxide, and the amount of hydrochloric acid liberated may readily be calculated as follows:

FIG. 1.



One gram-molecule, that is, 160 grams, of ferric oxide liberates six equivalents of hydrochloric acid. If these equivalents are present in 25 c.c., the normality is raised by 240. Thus 10 mg. of ferric oxide raise the normality by 0·015*N*. This amount is very appreciable in view of the low acidities used.

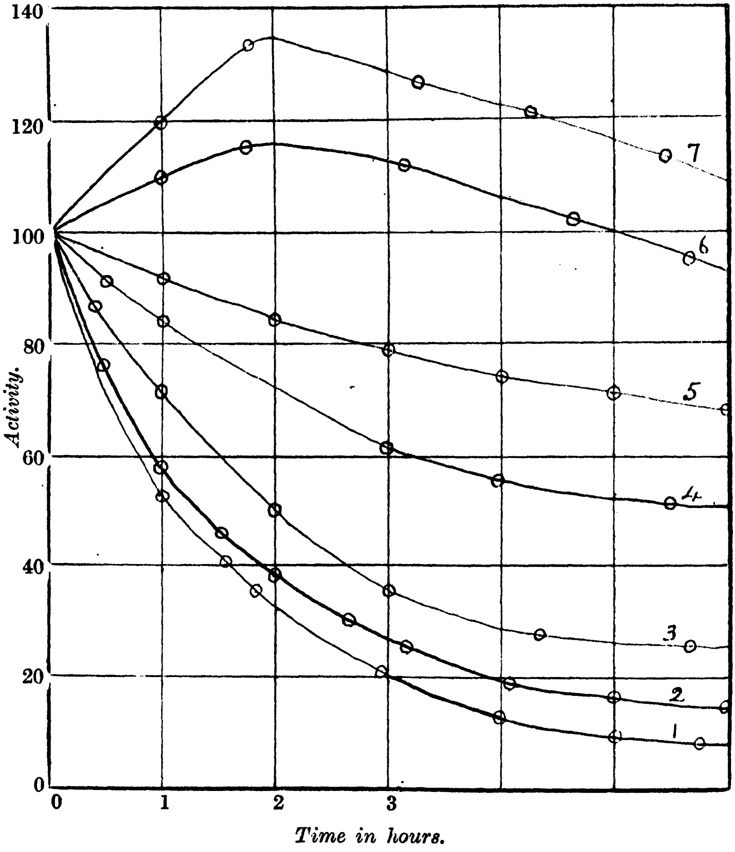
A second series of experiments was accordingly undertaken in which the actual concentration of hydrogen ion was measured in place of the normality of the hydrochloric acid. The active deposit was dissolved as before in hydrochloric acid of varying strength, fumaric acid and ferric chloride were added, and the iron was precipitated by boiling. The filtrate from each experiment was collected and the concentration of hydrogen ion in it determined by the hydrogen cell. The final acidity thus measured is a complex quantity, being the sum of three factors—the hydrochloric acid used, the fumaric acid added, and the hydrochloric acid liberated by the hydrolysis of the ferric chloride. It is therefore not strictly comparable with the figures in the previous table, which refer only to the normality of the hydrochloric acid used. Indeed, when the active deposit is removed from the plate by simply warming in ferric chloride solution without the addition of any acid, the resulting filtrate is distinctly acid. To reach lower acidities it is necessary to add dilute alkali to the ferric chloride, and care has to be taken to avoid local precipitation of ferric hydroxide during the addition.

The results of this series of experiments are given in the following table, and the decay curves obtained are shown in Fig. 2.

Final hydrion concentration in grams per litre	0·0085	0·0068	0·0063	0·0055	0·0049	0·0046	0·0037
Atomic ratio, Th-*B*/Th-*C*	1·2	2·25	3·8	7·8	10·6	13·9	16·9

The same transition from excess of the *C*-member to excess of the *B*-member is again evident, and Fig. 3 shows graphically the increase of the ratio Th-*B*/Th-*C* with diminishing acidity. The flat portions of the graph can be prolonged at either end, and experimental points have been obtained corresponding with higher and lower acidities than those shown. As the middle part of the graph is the most interesting, it only has been shown on a larger scale than would otherwise be possible. The top portion of this graph is the more difficult to realise experimentally, and in order to control better the lower acidities, an attempt was made to use the buffer mixtures of hydrochloric acid and sodium acetate given by Walpole (T., 1914, **105**, 2501, 2521). The active deposit was dissolved in a mixture of hydrochloric acid and sodium acetate having a known hydrion concentration, and ferric chloride added so as to precipitate basic ferric acetate as adsorbent. Unfortunately, with the low concentration of acetic anion in these mixtures and the small quantity of iron permissible as adsorbent, it was not found possible to precipitate basic ferric acetate at an acidity greater than [H$^{\cdot}$] = 10^{-6}. At this very low acidity thorium-*B* was adsorbed in large excess. At the lower end, the curve is limited by the strength of acid in which ferric hydroxide can be formed by hydrolysis. In no experiment was pure thorium-*C* adsorbed, the nearest approach to it being a mixture for which the atomic ratio Th-*B*/Th-*C* was 0·4. It should be noted that even when thorium-*B* and thorium-*C* are present in equal quantity, the decay curve for the mixture differs from that of pure thorium-*C* only very slightly

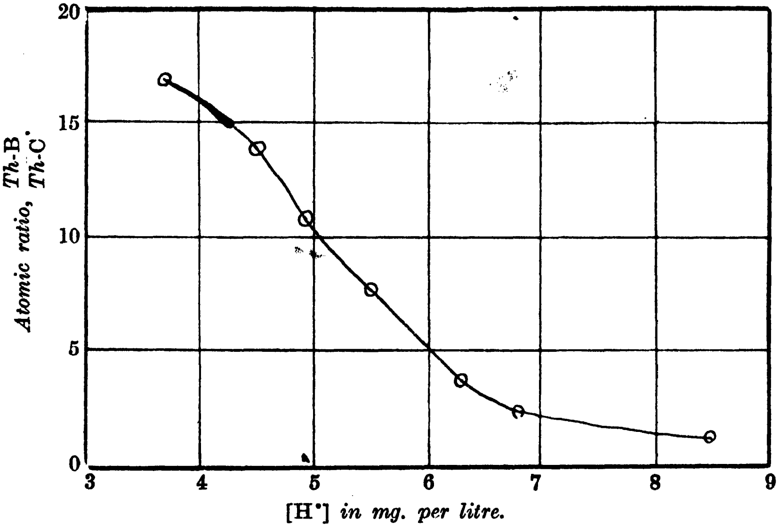
FIG. 2.



during the first three hours, and only after four hours does the difference due to the thorium-*B* become really appreciable.

It is worth while comparing the graph of Fig. 3 with that published by von Hevesy (*Phil. Mag.*, 1912, [vi], **23**, 628) in his investigation of the electrochemical properties of thorium-*B* and thorium-*C*, in which he deposited both these elements on metallic electrodes at varying potentials. By dipping a noble metal in a solution of one of its salts, for example, silver in silver nitrate, a positive potential was obtained; similarly by dipping such a metal as magnesium or zinc in a solution of its sulphate the electrode took up a negative potential towards the solution. At a positive potential thorium-*C* was deposited on the electrode almost pure, whilst at a sufficiently negative potential thorium-*B* was deposited in large excess; at intermediate potentials the two members were deposited in varying ratios, the proportion of thorium-*C* diminishing as the potential became more negative, and at — 0·6 volt against the calomel electrode the two were deposited in radioactive equilibrium. The graph showing the ratio of thorium-*B* to thorium-*C* as ordinate and the electrode potential as abscissa has the same general form as that of Fig. 3, and both curves show an inflexion at the point corresponding with the radioactive equilibrium.

FIG. 3.



The explanation of this similarity between the curves for electrodeposition and adsorption probably lies in the application of von

Lerch's rule, that the successive products in a disintegration series become more "noble," and in the fact that thorium-*B* and thorium-*C* are known to exist both as colloids and ions. Thorium-*B* exists as a negatively charged colloid and thorium-*C* as a mixture of negative and positive colloid, the amount of positive decreasing with the acidity of the solution. In very weakly acid solution both exist mainly as negative colloids. As the acidity gradually increases, it is suggested that thorium-*B*, as the less noble element, with the greater tendency to form positive ions, passes first into the ionic state, while thorium-*C* remains colloidal. Hence, in the most acid solutions, thorium-*C* is adsorbed almost pure by the positively charged ferric hydroxide, but as the acidity diminishes and thorium-*B* passes into the colloidal state, the latter is adsorbed in increasing ratio and finally in excess of the equilibrium ratio. This reasoning also explains why thorium-*B* cannot be adsorbed in the same high degree of purity as thorium-*C*, for in weak acid that part of the thorium-*C* which is present as negative colloid is adsorbed along with the thorium-*B*.

To test the validity of this colloidal theory a third series of experiments was undertaken in which colloidal ferric hydroxide was used. The active deposit was dissolved as before in 25 c.c. of hydrochloric acid, the strength of which was gradually diminished in successive experiments. Below about *N*/10,000-acid it is not possible to dilute hydrochloric acid with accuracy, and for these low acidities hydrochloric acid was replaced by mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate, for which the hydrogen-ion concentration is accurately known (see Prideaux, "Theory and Use of Indicators"). To the solution of the active deposit was added 1 c.c. of ferric hydroxide hydrosol (dialysed free from hydrochloric acid) and the iron was precipitated by addition of a drop of sodium sulphate solution. The precipitated iron carried down thorium-*B* and thorium-*C* in varying proportions, the relative amount of thorium-*B* increasing as before with diminishing acidity. The results are shown in the following table. The acidity of the solutions is given for convenience in the form of log $[\mathrm{H}^{\cdot}]$; thus, for *N*/100-acid, log $[\mathrm{H}^{\cdot}] = -2$.

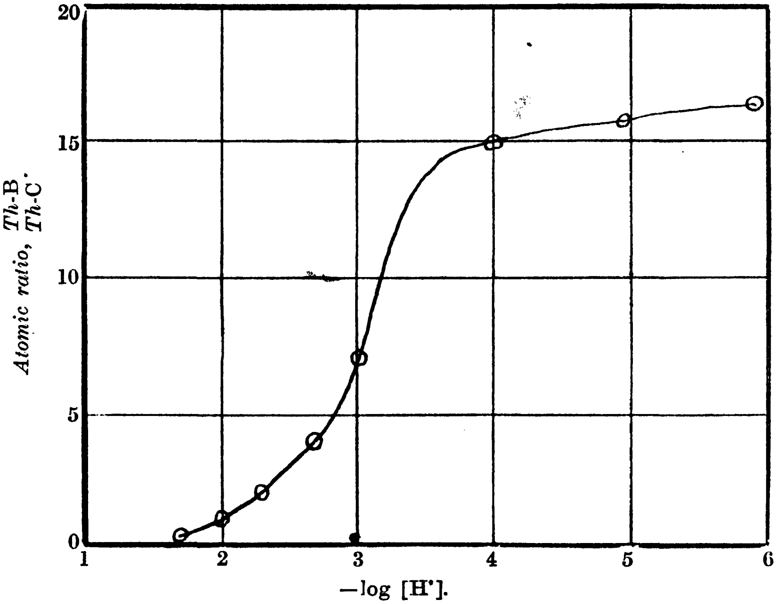
$-\log [\mathrm{H}^{\cdot}]$	1·7	2·0	2·3	2·7	3·0	4·0	4·94	5·91
Atomic ratio, Th-*B*/Th-*C*	0·45	0·97	2·0	3·5	7·0	15·0	15·6	16·2

The variation of the ratio of thorium-*B* to -*C* is shown in Fig. 4; the acid end of the curve is limited, of course, by the strength of the acid in which ferric hydroxide can be precipitated. Although not identical with the curve of Fig. 3, this graph shows the same general shape, with a well-defined transition from excess of the

C-member to excess of the *B*-, and has the same inflexion at the point of radioactive equilibrium.

These results obtained with colloidal iron appear to bear out the colloidal hypothesis previously outlined. Although the concentration of the radioactive matter is insufficient to coagulate the colloidal iron, once this coagulation is effected by addition of a suitable electrolyte the positively charged iron adsorbs that part of the radioactive matter which exists as negative colloid, the electric charges neutralising one other. The inflexion pointed out by von Hevesy and noted again in Figs. 3 and 4 is not so easily explained. Why should these curves, relating to different phenomena, both show an inflexion at the same point, and that the point corresponding with the radioactive equilibrium? One is tempted to look for some connexion between the electrical and colloidal properties of these elements and their atomic stabilities as expressed by their equilibrium ratio.

FIG. 4.



Further experiments are being carried out in order to obtain more data on this point.

Summary.

1. It has been shown that ferric hydroxide adsorbs thorium-*B* and thorium-*C* in proportions varying regularly with the acidity

of the solution. The method is suitable for separating pure thorium-*C* only if the acidity is kept above a certain limit.

2. The variation of the ratio of thorium-*B* and thorium-*C* is continuous, so that the effect seems to be true adsorption and not the formation of a chemical compound between the active matter and the iron.

3. A colloidal theory has been suggested to explain the experimental results; it involves the passage of the radioactive matter from the ionic to the colloidal state, the change being governed by the acidity of the solution.

4. A parallelism has been pointed out between the results reported here and those of von Hevesy for electrode deposition of the same elements. From this parallelism some evidence has been obtained that suggests a connexion between the atomic stabilities of thorium-*B* and thorium-*C* and their electrochemical properties.

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CCXXXV.—*Metallic Derivatives of Nitrophenolic Compounds. Part II. Some Nitrotolyloxides of Metals of Group II.*

By DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD.

IN the present communication, a study has been made of the salts derived from the 1 : 2 : 3-, 1 : 3 : 4-, 1 : 4 : 3-, and 1 : 3 : 6-nitrocresols, together with some compounds of dinitro-*o*-cresol. By comparing these with the alkaline-earth nitrophenoxides (Goddard, this vol., p. 1161), the change in solubility and in colour due to the influence of the methyl group is dealt with, and since the thalliumdialkyl nitrotolyloxides (Goddard, this vol., p. 1310) resemble the alkali compounds, they have also been alluded to in tracing similarities in solubility. All the substances now described were made by treating the nitrocresols in aqueous solution with the hydroxides or carbonates of the metals. The following hydrated barium salts have now been isolated: the 3-nitro-*o*-tolyloxide ($+ 2H_2O$); the 4-nitro-*m*-tolyloxide ($+ 1H_2O$); the 6-nitro-*m*-tolyloxide ($+ 6H_2O$), together with their anhydrous salts and the anhydrous 3-nitro-*p*-tolyloxide. The anhydrous salts were obtained by heating the hydrated forms at temperatures ranging from 120—160°. In the three cases, where the nitro- and hydroxyl groups are in the *ortho*-position to one another, the deepest colour is observed, this reaching a maximum in the compound having $CH_3 : OH : NO_2 = 1 : 2 : 3$. The difference, however, in colour between the compounds containing these groups in positions 1 : 3 : 4 and 1 : 4 : 3 is not so marked as in the corresponding thalliumdialkyl compounds, and all the salts are darker than barium *o*-nitrophenoxide.

Although the last-named salt has never been obtained with water of crystallisation, it is noticeable that two of the above salts have water of hydration, which may be associated in some way with the presence of the methyl group. Barium 3-nitro-*o*-tolyloxide is the most soluble of the three compounds, and more so than barium *o*-nitrophenoxide, but it is much more insoluble than the thalliumdialkyl derivatives. The 6-nitro-*m*-tolyloxide having its nitro- and hydroxyl groups in the *para*-position is comparable with barium *p*-nitrophenoxide, and it has almost the same solubility in organic solvents.

In the case of the strontium salts, the following were obtained: the 3-nitro-*o*-tolyloxide ($+ 2H_2O$); the 4-nitro-*m*-tolyloxide ($+ 4H_2O$); the 3-nitro-*p*-tolyloxide ($+ 4H_2O$), and their corresponding anhydrous derivatives, also the anhydrous 6-nitro-*m*-tolyloxide. A noticeable feature of the strontium salts is the differently coloured solutions they give when heated with the various solvents, this not being so marked with the barium and calcium compounds. They are more soluble in ethyl acetate than the barium salts, and the greatest solubility is again shown by the derivative of 1 : 2 : 3-nitrocresol. When the nitro- and hydroxyl-groups in these compounds are in the *ortho*-position, their colour shows much more of the red and less of the yellow than strontium *o*-nitrophenoxide, and the yellow of the 1 : 3 : 6 salts is deeper than that of strontium *p*-nitrophenoxide.

In dealing with nitrophenoxides, it was shown that the calcium compounds usually contain more water of crystallisation than those of barium or strontium, but this has not been found to prevail in the present case. The undermentioned and their anhydrous derivatives are now described: the 3-nitro-*o*-tolyloxide ($+ 2H_2O$); the 4-nitro-*m*-tolyloxide ($+ 3H_2O$); the 3-nitro-*p*-tolyloxide ($+ 1H_2O$); and the 6-nitro-*m*-tolyloxide ($+ 2H_2O$). The anhydrous compounds of the first three are differentiated from the barium and strontium analogues by their greater solubility in alcohol, but the 4-nitro-*m*-tolyloxide is decidedly the most insoluble in organic solvents. The 6-nitro-compound resembles very closely calcium *p*-nitrophenoxide, being insoluble in most organic media.

Only two magnesium hydrates and their anhydrous salts have been investigated, namely: the 4-nitro-*m*-tolyloxide (+ $4H_2O$) and the 3-nitro-*p*-tolyloxide (+ $3H_2O$). These are the most soluble compounds yet described, and their corresponding nitrophenoxides are at present under investigation. Their colour tends more towards orange than is the case with the barium, strontium, and calcium salts. Staedel (*Annalen*, 1883, **217**, 159) describes barium dinitro-*o*-tolyloxide (+ $3H_2O$), and Cazeneuve (*Bull. Soc. chim.*, 1897, [iii], **17**, 204) a barium salt (+ $2H_2O$) and also a calcium derivative (+ $1H_2O$) (*Compt. rend.*, 1897, **124**, 1130), but no investigator seems to have described the strontium salt. It has now been obtained along with its hydrate (+ $6H_2O$), and is much more soluble than the mononitro-compound and is orange in colour.

Passing to the second vertical series of group II, the colours change from brilliant orange in the magnesium dinitrotolyloxide, through orange-yellow of the zinc salt to brilliant yellow in the cadmium salt. This points to the colour change being due to the metal itself, and not to any acquisition of a quinonoid structure. The following hydrates and their anhydrous derivatives have now been obtained: magnesium dinitro-*o*-tolyloxide (+ $3H_2O$); the zinc and cadmium salts containing (+ $2H_2O$) and (+ $6H_2O$) respectively. Their solubility in organic solvents increases with increasing molecular weight. The solubilities of all compounds have been tested in alcohol, ether, acetone, chloroform, carbon tetrachloride, toluene, light petroleum, ethyl acetate, and pyridine.

EXPERIMENTAL.

Derivatives of 3-Nitro-o-cresol.—$C_{14}H_{12}O_6N_2Ba,2H_2O$, bright red needles, which darken in toluene, carbon tetrachloride, or chloroform [Found: N = 5·88 (5·84)*; Ba = 28·70 (28·72); H_2O = 7·62 (7·54) per cent.]. $C_{14}H_{12}O_6N_2Ba$, deep red [Found: N = 6·36 (6·33); Ba = 31·10 (31·07) per cent.]. $C_{14}H_{12}O_6N_2Sr,2H_2O$, orange-red needles, which become deep red in pyridine or alcohol and darken in acetone or ethyl acetate [Found: Sr = 20·93 (20·45); H_2O = 8·47 (8·41) per cent.]. $C_{14}H_{12}O_6N_2Sr$, brownish-red [Found: Sr = 22·87 (22·33) per cent.]. $C_{14}H_{12}O_6N_2Ca,2H_2O$, slender, orange-yellow needles becoming red in chloroform, carbon tetrachloride, or toluene [Found: N = 7·21 (7·36); Ca = 10·57 (10·52); H_2O = 9·54 (9·46) per cent.]. $C_{14}H_{12}O_6N_2Ca$, red [Found: N = 7·97 (8·12); Ca = 11·69 (11·62) per cent.].

Derivatives of 4-Nitro-m-cresol.—$C_{14}H_{12}O_6N_2Ba,1H_2O$, red needles

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* The figures in the brackets denote the theoretical percentages.

[Found: N = 6·08 (6·08); Ba = 29·71 (29·85); H_2O = 3·82 (3·91) per cent.]. $C_{14}H_{12}O_6N_2Ba$, deeper red [Found: N = 6·33 (6·33); Ba = 30·89 (31·07) per cent.]. $C_{14}H_{12}O_6N_2Sr,4H_2O$, shining, rhomboidal, orange plates, becoming red in carbon tetrachloride or chloroform [Found: Sr = 19·20 (18·86); H_2O = 15·63 (15·51) per cent.]. $C_{14}H_{12}O_6N_2Sr$, dark red [Found: Sr = 22·76 (22·33) per cent.]. $C_{14}H_{12}O_6N_2Ca,3H_2O$, golden-yellow needles darkening in toluene or ethyl acetate [Found: N = 7·04 (7·02); Ca = 10·83 (10·04); H_2O = 12·76 (13·55) per cent.]. $C_{14}H_{12}O_6N_2Ca$, deep yellow [Found: N = 8·07 (8·12) per cent.].

$$C_{14}H_{12}O_6N_2Mg,4H_2O,$$

pale orange [Found: Mg = 6·03 (6·06); H_2O = 17·84 (17·96) per cent.]. $C_{14}H_{12}O_6N_2Mg$, pale orange [Found: Mg = 7·33 (7·41) per cent.].

Derivatives of 6-Nitro-m-*cresol.*—$C_{14}H_{12}O_6N_2Ba,6H_2O$, bright yellow plates, which become deep yellow in carbon tetrachloride, chloroform, or light petroleum [Found: N = 4·93 (4·92); Ba = 24·97 (24·12); H_2O = 19·78 (22·49) per cent.].

$$C_{14}H_{12}O_6N_2Ba,$$

golden-yellow [Found: N = 6·14 (6·33); Ba = 31·10 (31·07) per cent.]. $C_{14}H_{12}O_6N_2Sr$, bright yellow granules [Found: Sr = 22·28 (22·33) per cent.]. $C_{14}H_{12}O_6N_2Ca,2H_2O$, bright yellow granules, which become deep yellow in toluene [Found: Ca = 10·40 (10·52); H_2O = 9·64 (9·46) per cent.]. $C_{14}H_{12}O_6N_2Ca$, deep yellow [Found: Ca = 11·50 (11·62) per cent.].

Derivatives of 3-Nitro-p-*cresol.*—$C_{14}H_{12}O_6N_2Ba$, red shining plates [Found: N = 6·34 (6·33); Ba = 31·27 (31·07) per cent.]. $C_{14}H_{12}O_6N_2Sr,4H_2O$, scarlet plates, which become deep red in toluene or chloroform and darken in carbon tetrachloride or light petroleum [Found: N = 6·12 (6·03); Sr = 19·17 (18·86); H_2O = 15·21 (15·51) per cent.]. $C_{14}H_{12}O_6N_2Sr$, deep red [Found: N = 7·39 (7·14); Sr = 22·61 (22·33) per cent.].

$$C_{14}H_{12}O_6N_2Ca,1H_2O,$$

slender, orange-yellow needles, becoming yellow in chloroform and red in toluene [Found: N = 7·79 (7·72); Ca = 11·07 (11·04); H_2O = 4·64 (4·97) per cent.]. $C_{14}H_{12}O_6N_2Ca$, red [Found: N = 8·16 (8·12); Ca = 11·61 (11·62) per cent.].

$$C_{14}H_{12}O_6N_2Mg,3H_2O,$$

flat, orange needles, which become red in toluene [Found: N = 7·23 (7·32); Mg = 6·77 (6·35); H_2O = 14·08 (14·07) per cent.]. $C_{14}H_{12}O_6N_2Mg$, red [Found: N = 8·42 (8·51); Mg = 7·39 (7·41) per cent.].

Derivatives of Dinitro-o-*cresol.*—$C_{14}H_{10}O_{10}N_4Sr,6H_2O$, brilliant yellow needles, becoming orange in ether or chloroform and darkening in toluene [Found: N = 9·56 (9·49); Sr = 14·67 (14·84); H_2O = 17·82 (18·31) per cent.]. $C_{14}H_{10}O_{10}N_4Sr$, deep orange [Found: N = 11·70 (11·61); Sr = 17·90 (18·17) per cent.].

$C_{14}H_{10}O_{10}N_4Mg,3H_2O$,

golden-yellow needles, becoming orange in carbon tetrachloride or toluene [Found: Mg = 5·11 (5·14); H_2O = 11·65 (11·42) per cent.]. $C_{14}H_{10}O_{10}N_4Mg$, brilliant orange [Found: Mg = 5·78 (5·81) per cent.]. $C_{14}H_{10}O_{10}N_4Zn,2H_2O$, orange-yellow granules [Found: N = 11·42 (11·29); Zn = 13·55 (13·17); H_2O = 7·29 (7·26) per cent.]. $C_{14}H_{10}O_{10}N_4Zn$, orange-yellow [Found: N = 12·30 (12·18); Zn = 14·60 (14·21) per cent.].

$C_{14}H_{10}O_{10}N_4Cd,6H_2O$,

brilliant yellow plates, becoming orange in toluene or chloroform [Found: Cd = 18·30 (18·27); H_2O = 17·82 (17·57) per cent.]. $C_{14}H_{10}O_{10}N_4Cd$, orange yellow [Found: Cd = 21·75 (22·16) per cent.].

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CCXXXVI.—*The Reaction between Persulphates and Silver.*

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THE action of solutions of persulphates on metallic silver was first noticed by Marshall (*J. Soc. Chem. Ind.*, 1897, **16**, 396), who found that the silver gradually went into solution and that at the same time a black deposit was formed, which he considered was a peroxide, AgO. The reaction was further investigated by Levi, Migliorini, and Ercolini (*Gazzetta*, 1908, **38**, i, 583), who noticed that acid was produced and put forward the equations:

$$(1)\ 2Ag + K_2S_2O_8 + H_2O \longrightarrow Ag_2O + K_2SO_4 + H_2SO_4$$

$$(2)\ Ag_2O + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2O$$

as representing the course of the reaction. The solution might thus remain neutral or become acid, according to the relative velocities of the reactions (1) and (2). By the action of persulphates upon silver nitrate solution, Marshall (*Proc. Roy. Soc. Edin.*, 1900, **23**, 168) obtained a similar black precipitate, which he considered was the same peroxide, but Austin (T., 1911, **99**, 262) concluded, on account of its high sulphate content, that it was a mixture of silver peroxide and silver persulphate, whilst Tarugi (*Gazzetta*, 1902, **32**, ii, 383) considered it to be the silver salt of Caro's acid, namely, Ag_2SO_5.

There is some doubt as to the composition of silver peroxides, which are usually obtained, mixed or combined with salts, as anodic deposits in the electrolysis of solutions of silver salts in a divided cell. For example, by the use of silver nitrate solution a black, crystalline powder of metallic appearance is obtained (Ritter, *Gehlen's neues J.*, 1804, **3**, 561), which, on washing, immediately commences losing oxygen, silver nitrate being set free and passing into solution. The undecomposed crystals have the empirical formula $Ag_7O_{11}N$ (Sulc, *Zeitsch. anorg. Chem.*, 1896, **12**, 89; Tanatar, *ibid.*, 1901, **28**, 331) and later work has shown that they are very probably a double compound corresponding with the formula $AgNO_3,2Ag_3O_4$ (Babarovský and Kužma, *Zeitsch. physikal. Chem.*, 1909, **67**, 48; Brown, *J. Physical Chem.*, 1916, **20**, 680). Since oxygen is lost during the washing, the original peroxide may, however, contain a higher proportion of oxygen; on the other hand, from the anodic decomposition curves of both nitrate and sulphate solutions, Bose (*Zeitsch. anorg. Chem.*, 1905, **44**, 237) concluded that the oxide was Ag_2O_2.

In opposition to the view that these substances are double compounds of a peroxide of silver and ordinary silver salt—the peroxides are never obtained pure by this method—Watson (T., 1906, **89**, 578) concluded that the black silver deposit $Ag_7O_{11}N$ was a "peroxynitrate," that is, a definite compound, since he obtained it under varying conditions. He found that, on boiling, the dioxide, Ag_2O_2, was formed, and he described the properties of this and verified its composition.

In the course of some experiments on the action of persulphates on the photographic negative, it was necessary to investigate the action of persulphate on silver, both in the metallic and the ionic form, and it has been found that sodium or potassium persulphate solution converts metallic silver into a peroxide containing a greater proportion of oxygen than corresponds with the formula Ag_2O_2, whilst the acidity of the solution at the same time increases. When a strong (20 per cent.) solution of the sodium salt is used, the peroxide can rapidly be obtained in quantity, but owing to the much smaller solubility of the potassium salt the reaction with this is much slower (for example, eighteen hours) and the yield much lower, for the peroxide is unstable and decomposes continuously from the time of its formation. With the ammonium salt, no peroxide is formed, but the ammonium radicle is oxidised to nitric acid (compare Marshall and Ingliss, *Proc. Roy. Soc. Edin.*, 1902, **24**, 88). When the reaction is continued for more than about one hour, the product is contaminated with sulphate, which is always present to a slight extent.

It has been found that the same peroxide is produced when persulphates react with silver nitrate, again with increase in acidity, but in this case the contamination with silver sulphate is greater.

An explanation of this contamination has been found in the catalytic decomposition of persulphates by silver ions, previously noticed by Marshall in the case of the ammonium salt, whereby in the case of the sodium and potassium salts the reaction

$$S_2O_8'' + H_2O \longrightarrow 2HSO_4' + O$$

is immensely accelerated. The HSO_4' ions thus formed react continuously with silver ions, and as these are present in much greater quantity when silver nitrate is used, the amount of silver sulphate formed is consequently greater in this case. Moreover, the catalytic effect increases with increase of concentration of the silver ions, and this again tends to produce more contamination when silver nitrate is used in the preparation. A possible explanation of this catalytic effect is the intermediate formation of silver persulphate, which then immediately reacts with the water:

$$Ag_2S_2O_8 + H_2O \longrightarrow Ag_2SO_4 + 2H^{\bullet} + O + SO_4''.$$

As might be expected, it has been found that the presence of an oxidisable substance, such as gelatin, prevents the formation of peroxide, whilst it is itself oxidised; but it does not prevent the catalytic decomposition of the persulphate, with formation of acid sulphate. The application of this result to the action of persulphate as a photographic reducer is obvious, and will be discussed in another place.

EXPERIMENTAL.

Preparation of the Peroxide from Sodium Persulphate.

Metallic silver was obtained in the finely divided, crystalline form by precipitation from silver nitrate with metallic magnesium (compare Dodgson, *Phot. Jour.*, 1911, **51**, 265). The excess of magnesium was removed with dilute sulphuric acid, and the silver, which was of a grey colour, and in the form of crystals about 0·001 mm. in length, thoroughly washed by decantation. About 3 grams of this were introduced, wet, into a solution in 100 c.c. of water of 20 grams of sodium persulphate. This was the purest commercial product, but was considerably contaminated with acid sulphate, due to decomposition. It was not purified—a difficult matter—since acid sulphate is rapidly formed again during the reaction. The mixture was then stirred mechanically. It almost immediately darkened and after half an hour the grey silver appeared to have been converted into a black powder, whilst at the same time the acidity of the mixture increased. It was found that the solid consisted of a peroxide, with a considerable amount of unconverted silver, which usually persisted after the reaction had continued for an hour or more. Since the sulphate content rises with increase of time of reaction, the product, when free from silver, was contaminated with silver sulphate. It was washed with dilute sulphuric acid and water, and obtained as a black, metallic-looking powder, which, after drying on a porous tile over calcium chloride, lost its metallic appearance and finally resembled manganese dioxide. It decomposed continuously from the time of its formation, whether wet or dry, losing oxygen and becoming alkaline owing to the formation of silver oxide.

The substance thus obtained exhibits all the properties of the dioxide described by Watson; for example, it gives deeply coloured solutions with concentrated nitric acid or concentrated sulphuric acid, which decompose with loss of colour, gradually at the ordinary temperature, and rapidly on heating. It is, as might be expected, a strong oxidising agent; for example, it liberates iodine from acidified potassium iodide and converts quinol in acid solution into *p*-benzoquinone.

The same procedure was carried out in 5 per cent. gelatin solution. No peroxide was formed, although the silver gradually dissolved and the solution became strongly acid.

Analysis of the Product.

From numerous analyses it became evident that the more rapidly the product was removed from the filter and analysed, the higher was the percentage of the available oxygen. Since a period of a few minutes is sufficient substantially to alter the amount of oxygen, it seems that the analyses by Austin and by Watson (*loc. cit.*) of the dried products are of doubtful value.

To ascertain, if possible, towards what limit this available oxygen tended, experiments were made in which the washing of the product was carried out with ice-cold acid and water, in order to retard the decomposition. No evolution of gas was apparent under these conditions, but the procedure does not avoid decomposition during the formation of the peroxide, which cannot conveniently be carried out at 0° owing to the slowness of reaction at this temperature.

The analyses were made according to the method of Babarovský and Kužma (*loc. cit.*), the product being thrown wet into a known quantity of *N*/10-oxalic acid and an excess of 2*N*-sulphuric acid, and rapidly stirred to promote reaction with the oxalic acid, which was oxidised to carbon dioxide. Solution was completed by heating to boiling and the excess of oxalic acid estimated by titration with permanganate. The slight excess of this was then removed by oxalic acid, and after cooling, the silver estimated by Volhard's thiocyanate method.

Results of Analyses.—The ratio is that of atoms of total oxygen to atoms of silver, that is, it would be 1 for Ag_2O_2, and 1·33 for Ag_3O_4.

Preparation.	Time of keeping. (days).	Conditions.	Ratio.
No. 62	6	Exposed to air.	0·777
	,,	Kept over $CaCl_2$.	0·735
	11	,, ,, ,,	0·718
No. 63	0	Taken wet from the filter.	1·047
	,,	,, ,, ,,	1·044
	,,	,, ,, ,,	1·033
	1	Kept over $CaCl_2$.	0·965
No. 66	0	Washed at 0° and taken wet from the filter.	1·245
			1·251
			1·185
No. 70	,,	,, ,, ,,	1·29
			1·29

These results show that the undecomposed peroxide contains more oxygen than corresponds with the formula Ag_2O_2, but on no occasion was quite sufficient oxygen obtained to justify the formula Ag_3O_4.

Mechanism of the Reaction.

The explanation of Levi, Migliorini, and Ercolini, that the increase of acidity is due to the formation of sulphuric acid and undissolved silver oxide simultaneously, is obviously unsatisfactory; the acidity must arise from the decomposition of water during the reaction, the oxygen going to form the silver peroxide, while the hydrogen gives acid sulphate :

$$S_2O_8'' + H_2O \longrightarrow 2HSO_4' + O.$$

It should therefore be possible to trace the course of the reaction by determining the ratio between the increase of acidity and the quantity of silver converted into peroxide. Unfortunately, oxygen is invariably evolved during the reaction, either from actual decomposition of peroxide already formed, or directly from the reaction between the persulphate and water, this reaction being, as will be shown below, catalysed by silver ions, and this method is useless. If the peroxide has the formula Ag_3O_4, the reaction must be of the form

$$3Ag + 4S_2O_8'' + 4H_2O \longrightarrow Ag_3O_4 + 8HSO_4' .$$

and the increase of acidity is considerable in comparison with the silver dissolved.

When an oxidisable substance is present, the peroxide apparently reacts with this at once, for the silver goes into solution without any production of black peroxide, as may easily be demonstrated by mixing the persulphate solution with a gelatin solution containing colloidal silver.

This requires a reaction of the form

$$2Ag_3O_4 + 8HSO_4' \longrightarrow 6Ag^{\cdot} + 2HSO_4' + 6SO_4'' + 3H_2O + 5O \text{ (used in oxidation)}$$

and therefore the complete reaction for the solution of silver in persulphate when an oxidisable substance is present must be of the form

$$6Ag + 8S_2O_8'' + 5H_2O \longrightarrow 6Ag^{\cdot} + 6SO_4'' + 10HSO_4' + 5O,$$

a reaction considerably more complex than any that has been previously proposed, and further complicated by the fact that the persulphate ion alone may react directly with the water.

Preparation of the Peroxide from Silver Nitrate.

Sodium persulphate, although invariably contaminated with acid sulphate, gave much better results than the slightly soluble potassium salt used by Austin, since the more dilute solutions favoured decomposition.

Ten grams of silver nitrate dissolved in 10 c.c. of water, and 8 grams of sodium persulphate in 60 c.c. of water, were cooled to 0°, and the solutions rapidly mixed, the mixture being kept cold in ice. There was an immediate, grey precipitate formed, which was collected at once in a Gooch crucible, and on analysis was found to consist of almost pure silver sulphate containing only a slight trace of available oxygen. The filtrate, on keeping at 0°, commenced to throw down a black precipitate in less than five minutes; after fifteen minutes the precipitation appeared to be complete, and the product was collected, washed with ice-cold water, and analysed immediately. It was found to contain a large percentage of sulphate, but otherwise exhibited all the reactions of the peroxide, and appeared to be a mixture of silver peroxide and silver sulphate.

Analysis of the Product.

The analysis was carried out on two separate portions. In one portion the ratio of available oxygen to silver was obtained as described above, and in the other portion the ratio of sulphate to silver was determined by decomposing the product with hydrochloric acid, removing the silver as chloride, and estimating the sulphate in the filtrate as barium sulphate. From these two ratios it is possible to calculate the value of x when the formula is expressed as $Ag_2SO_4,(AgO_x)_n$, that is, the formula of the admixed peroxide.

Preparation No. 79.—The peroxide–sulphate mixture was prepared at 0° as described above, and washed four times with water at 0°. Two determinations were made of the ratio of available oxygen to silver, the mean being taken, and one of sulphate to silver. Formula calculated: $Ag_2SO_4,(AgO_{1\cdot295})_{1\cdot654}$, that is, the product is a mixture of 1 part of silver sulphate with 1·654 parts of a peroxide containing slightly less oxygen than corresponds with the formula Ag_3O_4.

A similar determination of another preparation gave the result $Ag_2SO_4,(AgO_{1\cdot287})_{1\cdot59}$, and there seems to be little doubt that the precipitate is a mixture of peroxide and sulphate.

Catalysis by Silver Ions of the Decomposition of Persulphates.

From experiments with mixtures of solutions of silver nitrate and of neutral sodium or potassium persulphate it was found that the acidity increased continuously from the time of mixing. It was therefore obvious that the decomposition of persulphates in solution, namely, $S_2O_8'' + H_2O \longrightarrow 2HSO_4' + O$, is catalysed by the silver ions, since this decomposition takes place only very slowly at the ordinary temperature with neutral solutions (Green and Masson, T., 1910, **97**, 2083). The extent of this catalysis was determined for potassium persulphate, which is the most convenient salt to obtain pure.

A $N/20$-solution of potassium persulphate, with additions of silver nitrate, was maintained at 18° and estimations made of the acidity of portions removed at known intervals after the addition of the silver. To render the acidimetry possible without formation of silver oxide, the solution to be tested was run into an amount of sodium chloride solution rather greater than that necessary to convert all the silver into silver chloride.

Since the reaction can be only approximately monomolecular owing to the side reaction with the silver, the values of $\frac{1}{t}\log_e\frac{a}{a-x} = k$, the velocity constant, were found to be somewhat irregular, but when the formula $k = \frac{1}{t-t_1}\log_e\frac{a-x_1}{a-x}$ was employed, where t_1 was about five minutes, the constancy was reasonably good, errors due to the side reaction being eliminated, as the following results for $N/250$-concentration of silver nitrate indicate. Temperature 18°; a, the original concentration of persulphate expressed as c.c. of standard alkali, is 24·25.

t in mins.	x = c.c. of alkali required for neutralisation.	$k = \frac{1}{t-6}\log\frac{a-0{\cdot}2}{a-x}$.
2	0·05	—
6	0·2	—
11	0·3	0·0008
30	0·8	0·0010
60	1·3	0·00086
90	1·7	0·00077
150	2·4	0·00066
195	3·05	0·00067
		Mean 0·00079

The results of this and similar experiments are as follows: Temperature 18°. Concentration of potassium persulphate = $N/20$. c = concentration of silver nitrate.

c.	k.	k/c.
$N/250$	0·00079	0·20
$N/100$	0·0021	0·21
$N/50$	0·00375	0·19

These results show that the catalysed decomposition of the persulphate is an approximately monomolecular reaction, and that the velocity of decomposition is approximately proportional to the concentration of the silver ion.

The author desires to express his thanks to Dr. Slater Price for the interest he has taken in this work, and for his valuable advice and criticism.

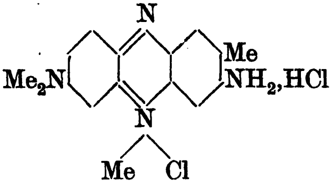
THE BRITISH PHOTOGRAPHIC RESEARCH
ASSOCIATION LABORATORY.

[*Received, October 20th,* 1921.]

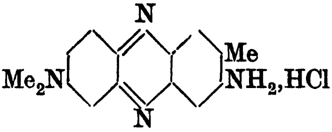
CCXXXVII.—*Structure and Colour of the Azine Scarlets.*

By JULIUS BEREND COHEN and HERBERT GRACE CRABTREE.

IN connexion with an inquiry into the antiseptic action of certain dyestuffs undertaken for the Medical Research Council, it was found necessary to examine specimens of Azine Scarlets which resemble in structure the yellow dye acriflavine, well known as an antiseptic. In Green's edition of " Organic Colouring Matters " by Schultz and Julius (1904) it is stated on p. 228, under No. 582, that Azine Scarlet G (the only one mentioned) is obtained by the action of nitrosodimethylaniline on *m*-aminodimethyl-*p*-toluidine, and has the following formula (I):



Azine Scarlet G.
(According to S. and J.)
(I.)



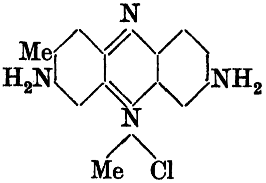
Toluylene Red.
(II.)

According to this formula, Azine Scarlet G appears as the methochloride of Toluylene Red (II).

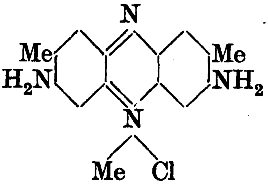
If, however, the preparation is carried out according to the directions given under a patent by Meister, Lucius, & Brüning, No. 69188, or if Toluylene Red is converted into the methochloride, the same colouring matter is apparently formed; but instead of the scarlet dye known commercially as Azine Scarlet G, a substance is produced in both cases which has a bright magenta colour.

In the patent literature on the subject there are several methods given for preparing scarlet dyes of the phenazine group. Thus, Friedländer ("Fortschritte der Teerfarbenfabrikation," Vol. IV, p. 376) mentions a patent, No. 80758 by Meister, Lucius, & Brüning "for preparing red basic azine dyes" from nitroso-mono- or -di-methyl-*o*-toluidine, nitroso-mono- or -di-ethyl-*o*-toluidine, and *m*-aminodimethyl-*p*-toluidine, and in the same volume (p. 380) there is a further patent, No. 86608, by the Farbwerke Mühlheim, "for preparing scarlet dyes of the safranine group" by heating *p*-aminoazo-compounds with *o*-aminodimethyl-*p*-toluidine. A number of these compounds have now been prepared, from which it appears that the substitution of methyl and other radicles for hydrogen in the amino-group produces a change of tint from scarlet to magenta—in other words, the introduction of the heavier auxochrome group causes a displacement of tint towards the blue end of the spectrum.

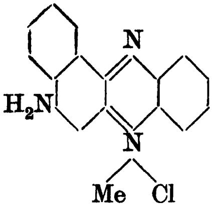
Thus, the following series of aminophenazine salts of the methochlorides have a scarlet colour:

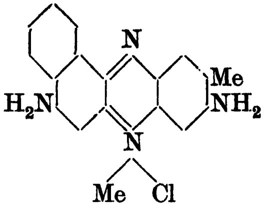


(III.)

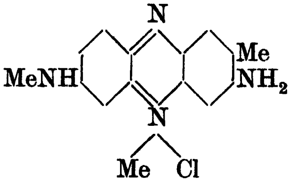


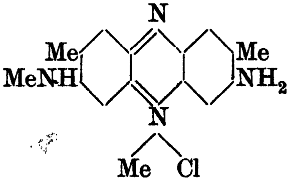
(IV.)

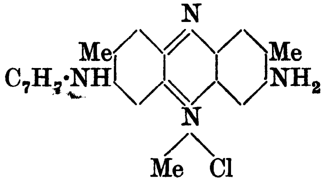

(V.)


(VI.)

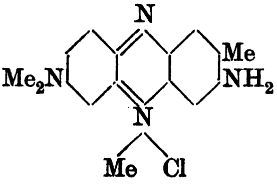
The following have a bluer tint intermediate between scarlet and magenta :

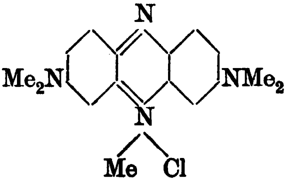

(VII.)

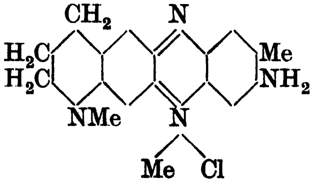

(VIII.)


(IX.)

Whereas the following three compounds have a magenta or bluish-red tint.

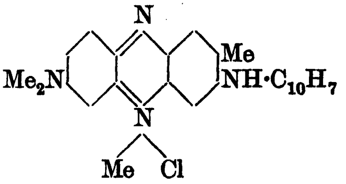

(X.)


(XI.)

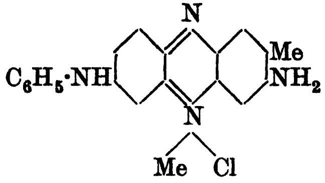

(XII.)

Further examples of the shifting of tint towards the blue by the introduction of heavier radicles into the amino-group are illustrated

by the dye described under D.R.-P. 89659 by Meister, Lucius, & Brüning (Friedländer, *op. cit.*, Vol. IV, p. 379), which has probably the following formula (XIII); it dissolves in water with



(XIII.)



(XIV.)

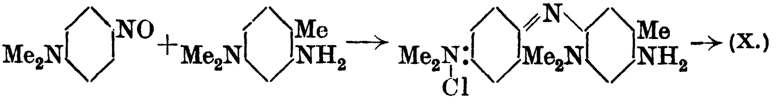
a bluish-violet and in alcohol with a reddish-violet colour; and by the dyestuff (XIV) described in D.R.-P. 85231 (Friedländer, *op. cit.*, Vol. IV, p. 377), which dissolves with a violet colour.

The same shifting of tint towards the blue is observed in rosaniline and in its methyl and phenyl derivatives, which show a similar gradation from magenta to violet and blue by the introduction of heavier radicles into the amino-group.

EXPERIMENTAL.

3-*Amino*-7-*dimethylamino*-2-*methylphenazine Methochloride*.

The colouring matter described in Green's edition of "Organic Colouring Matters" by Schultz and Julius (1904) as Azine Scarlet G (formula X) has been prepared by three methods. (1) One method (given by Schultz and Julius) is that described in D.R.-P. 69188 (Friedländer, *op. cit.*, Vol. III, p. 397) by the action of nitrosodimethylaniline upon 2-aminodimethyl-*p*-toluidine according to the reaction:



(*Indamine.*)

It will be seen that in passing from the indamine to the final stage a methyl group is eliminated from the dimethylamino-group.

The 2-aminodimethyl-*p*-toluidine was obtained by the nitration of dimethyl-*p*-toluidine and subsequent reduction with stannous chloride and hydrochloric acid. The latter, recrystallised from light petroleum, formed large prisms, m. p. 55°.

Fifteen parts of the base were dissolved in 100 parts of 50 per cent. acetic acid, and 18·6 parts of *p*-nitrosodimethylaniline hydrochloride added. A transient green coloration due to the formation of the intermediate indamine was immediately succeeded, on warming on the water-bath, by a deep blue, which changed to magenta after two or three hours' heating. The whole was diluted with 200 parts of water, filtered hot, and the colouring matter precipitated with sodium chloride and zinc chloride.

(2) The second method consisted in converting Toluylene-red into the methochloride. The red dye was prepared according to Witt's method (*Ber.*, 1879, **12**, 931) by mixing 3·6 grams of *p*-nitrosodimethylaniline hydrochloride with 2·4 grams of *m*-tolylenediamine, each dissolved in 50 c.c. of water at 30°, and allowing the mixture to stand over-night. The dark green indamine was filtered, pressed, dissolved in 100 c.c. of water, and boiled for three hours, when a drop on filter-paper gave only a faint blue rim. The solution was filtered and the dye salted out. When recrystallised from alcohol, it formed a brown, microcrystalline powder.

The colouring matter was acetylated by heating 5 grams with 15—20 grams of acetic anhydride and 2—3 grams of fused sodium acetate: having been poured into water, the acetyl derivative was precipitated with sodium hydroxide, filtered, and crystallised from alcohol. It formed brown plates. Two grams of the acetyl derivative were dissolved in 5 grams of nitrobenzene heated at 170° and 0·9 gram of methyl-sulphate was added. The heating was continued for a minute and the product cooled. The brownish-black solid which separated was filtered, washed with ether, dried, and boiled with 10 c.c. of concentrated hydrochloric acid for half an hour. A deep blue solution was formed, which was poured into water, when the colour changed to bright magenta. The methochloride was salted out and formed a semi-solid, iridescent, green mass, which after drying became hard and when crystallised from a mixture of benzene and alcohol formed a microcrystalline powder with a dark green lustre (Found: N = 17·0. $C_{16}H_{20}N_4Cl_2$ requires N = 16·5 per cent.).

The products obtained by the two methods gave identical colour reactions with alkalis and acids, as described in the patent (*loc. cit.*).

According to the first method, the change from indamine to the final stage takes place with the elimination of a methyl group from the dimethylamino-group.

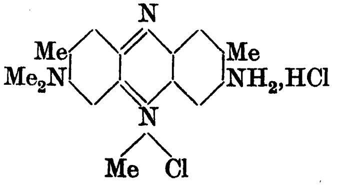
(3) In order to obtain further evidence on this point, a third method was adopted for preparing the colouring matter, namely, from nitrosodimethylaniline hydrochloride and the 2-aminomonomethyl-*p*-toluidine, in which case hydrogen would be eliminated in place of a methyl group. Monomethyl-*p*-toluidine was prepared by Ullmann's method (*Annalen*, 1903, **327**, 165). One hundred and thirty grams of *p*-toluidine were dissolved in 180 c.c. of ether in a flask provided with a reflux condenser, and 99 grams of methyl

sulphate were run in during ten minutes. Heat was developed and the flask was cooled with water. The methosulphate, $CH_3 \cdot C_6H_4 \cdot NH(CH_3),CH_3 \cdot HSO_4$, rapidly formed and in a short time the contents of the flask became nearly solid. Water was added, the ether layer separated, and the aqueous layer further extracted. The ether was removed without dehydrating and the crude base purified by conversion into the nitroso-derivative and subsequent reduction. The crude base was dissolved in 150 c.c. of concentrated hydrochloric acid and 500 c.c. of water, cooled to 0—5°, and a solution of 45 grams of sodium nitrite slowly run in. A nearly colourless nitrosomethyl-*p*-toluidine separated and was filtered, washed with water, and dried on a porous plate. The product (42 grams; m. p. 53°) was dissolved in a minimum quantity of alcohol and a solution of 130 grams of stannous chloride in 200 c.c. of concentrated hydrochloric acid added gradually with shaking. After heating on the water-bath for half an hour, the whole was made alkaline and distilled in steam. Sodium chloride was added to the distillate and the base extracted with ether. The ether solution was dehydrated over potassium hydroxide and the ether removed. The residue distilled at 200°. The yield was 16 grams, or 48 per cent. of the theoretical. The nitration of the base was carried out as described by Pinnow (*Ber.*, 1895, **28**, 3040). The yield was theoretical. The substance crystallises in large, red prisms, m. p. 59°. The reduction was effected with stannous chloride. Thirty-one grams of stannous chloride were dissolved in 50 c.c. of concentrated hydrochloric acid and 5 grams of the nitro-base added slowly. Rapid reduction and decolorisation of the substance took place, after which the mixture was heated for half an hour on the water-bath. The solution was then made alkaline and the base extracted with ether. The ether extract was dehydrated and the ether removed. The 2-aminomonomethyl-*p*-toluidine remained as a pale brown oil, which was used without further purification. A mixture of 3·4 grams of the base, 4·6 grams of *p*-nitrosodimethylaniline hydrochloride, and 25 grams of 50 per cent. acetic acid was heated on the water-bath for three hours until a sample diluted with water and dropped on filter-paper gave only the faintest suggestion of blue on the rim of the spot. It was then diluted, filtered, and the colouring matter salted out with sodium and zinc chlorides. The product appeared to be identical in every respect with those prepared by the two previous methods.

3-*Amino*-7-*dimethylamino*-2 : 8-*dimethylphenazine Methochloride*.

The *p*-dimethylamino-*o*-toluidine required was obtained by coupling dimethyl-*o*-toluidine with diazotised sulphanilic acid, a process which is effected exactly as in the preparation of methyl-orange, except that the operation is conducted at room temperature. Dimethyl-*o*-toluidine (1 mol.) is exactly neutralised with hydrochloric acid diluted with about four times its weight of water. Sulphanilic acid (1 mol.) is dissolved in an equivalent of sodium carbonate solution (15 parts of water to 1 part of sulphanilic acid), and sodium nitrite (1 mol.) dissolved in water added, the whole being acidified with hydrochloric acid (2·1 mols.). The hydrochloride of the base in solution having been added to the diazo-solution, the mixture is made slightly alkaline with a few c.c. of sodium hydroxide solution and stirred for four hours, when the colouring matter is thrown down in orange leaflets. It is filtered, washed with concentrated brine, and dried at 50°. It was reduced by adding to the substance dissolved in an excess of boiling hydrochloric acid zinc dust until completely decolorised. It was then cooled, filtered, neutralised with sodium hydroxide, and the base extracted with ether. The ether extract was dehydrated with potassium hydroxide and the ether removed. A pale brown oil remained which soon solidified, and was used without further purification. The same substance is described by Bernthsen (*Ber.*, 1892, **25**, 3128), who obtained it by nitrating *o*-toluidine, methylating the product, and finally reducing the nitro-group, but the above method was found to be much more convenient and more easily carried out.

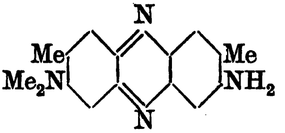
Sixteen parts of *p*-dimethylamino-*o*-toluidine and 15 parts of 6-dimethylamino-*m*-toluidine were dissolved in 300 parts of water, 20 parts of concentrated hydrochloric acid, and 30 parts of 50 per cent. acetic acid, and cooled to 10° with stirring. Thirty parts of sodium dichromate in 400 parts of water were run in during three hours. A bluish-red coloration developed immediately and became more intense as the oxidising agent was added. The mixture was finally warmed on the water-bath for an hour, filtered, and salted out with zinc chloride and sodium chloride. The product was purified by solution in water, filtration, and reprecipitation with salt solution. It could not be recrystallised from alcohol or dilute hydrochloric acid. The substance, by analogy with the formation of tetramethyldiaminophenazine (p. 2064), has the following structure:



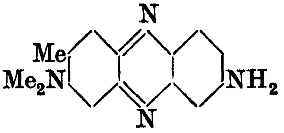
(XV.)

It dissolves in water with a magenta colour similar to that of Toluylene-red methochloride.

Attempts to prepare



and



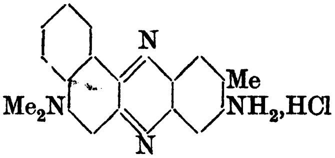
by condensing by the above reaction the *p*-diamine with *m*-phenylene- and *m*-tolylene-diamine were unsuccessful. With tolylenediamine, a dark brown coloration rapidly developed and assumed a dirty red colour at a later stage, a mass of sticky, dark brown crystals being deposited, which could not be purified.

5-*Aminonaphthaphenazine* 7-*Methochloride* (Formula V).

This substance was prepared according to the method described by O. Fischer and Hepp (*Ber.*, 1890, **23**, 845) by heating in a sealed tube for five to six hours at 160° *o*-phenylenediamine (1 mol.) and benzeneazo-α-naphthylamine hydrochloride (1 mol.) with 10 parts of alcohol. On cooling, dark red crystals separated. They were filtered and crystallised from alcohol containing hydrochloric acid. The substance obtained in this way is the hydrochloride of aminonaphthaphenazine. It forms dark red crystals which are slightly soluble in water, but on heating are hydrolysed and the base is precipitated. The acetyl derivative was obtained by heating the base with acetic anhydride and fused sodium acetate. On cooling, the acetyl derivative crystallised. It was heated at 160° with ten to twenty times its weight of nitrobenzene and the equivalent of 1 molecule of methyl sulphate added. On standing, crystals of the methosulphate separated. They were filtered, washed with ether, and heated with concentrated hydrochloric acid, when the methochloride slowly crystallised in dull red, microscopic crystals. The substance dissolves in water with a bright scarlet colour like the hydrochloride, $C_{17}H_{14}N_3Cl,HCl$, but is not so readily hydrolysed as the latter.

9-*Amino*-5-*dimethylamino*-10-*methylnaphthaphenazine* *Hydrochloride*.

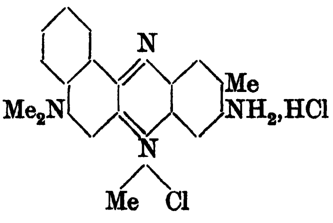
The 4-nitrosodimethyl-α-naphthylamine hydrochloride required in this preparation is described by Friedländer and Welmans (*Ber.*, 1888, **21**, 3123). The reaction goes smoothly and the yields of both base and nitroso-derivative are nearly theoretical. The latter is less soluble than the corresponding nitrosodimethylaniline, and therefore it is difficult to isolate the intermediate indamine in aqueous solution. 2·3 Grams of nitrosodimethylnaphthylamine hydrochloride were dissolved in 20 c.c. of hot glacial acetic acid, to the solution 1·2 grams of *m*-tolylenediamine dissolved in 20 c.c. of 50 per cent. acetic acid and 1 c.c. of concentrated hydrochloric acid were added, and the mixture was heated on the water-bath for four hours. A magenta colour developed rapidly, losing its blue tint on continuous heating and becoming more crimson in shade. The solution was finally boiled, diluted with 100 c.c. of water, filtered, and the hydrochloride of the dye precipitated with brine. It was purified by redissolving it in water and reprecipitating with brine. A considerable amount of by-product was formed during the reaction, which was still more noticeable when *m*-phenylenediamine was used in place of the tolylenediamine. The colouring matter prepared as described is not very soluble in water, but dissolves in alcohol. It forms a black, shining powder which dissolves in water with a magenta colour similar to that of Toluylene-red methochloride. It has probably the following formula :



(XVI.)

9-*Amino*-5-*dimethylamino*-10-*methylnaphthaphenazine Methochloride.*

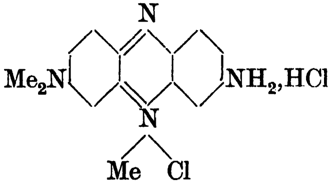
The process was conducted as described above, but the *m*-tolylenediamine was replaced by *p*-dimethylamino-*o*-toluidine. 2·4 Grams of 4-nitrosodimethyl-α-naphthylamine hydrochloride, dissolved in 20 c.c. of glacial acetic acid, were added to 1·5 grams of the dimethylamino-*o*-toluidine in 20 c.c. of 50 per cent. acetic acid and 1 c.c. of concentrated hydrochloric acid. A bright crimson colour developed rapidly, and after three hours' heating on the water-bath the dye was separated and purified as in the previous case. The hydrochloride of this colouring matter is even less soluble than the above hydrochloride, but is readily soluble in alcohol. The formula may be represented as follows :



(XVII.)

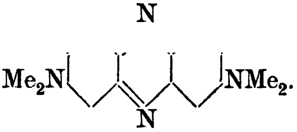
3-*Amino*-7-*dimethylaminophenazine Methochloride.*

This compound, which has been described by Karrer (*Ber.*, 1916, **49**, 1643; 1917, **50**, 420), was prepared in order to compare the effect on the colour caused by the absence of methyl groups in the nucleus of the two benzene rings. It was obtained by oxidising a mixture of dimethyl-*p*- and -*m*-phenylenediamine with potassium dichromate. The phenazine salt was salted out by zinc and sodium chlorides, from which the base was precipitated by the addition of sodium hydroxide or ammonia. It dissolves in alcohol and in dilute acid with a deep violet colour.



It is the methochloride of "Neutral-violet," which has a similar tint. The absence of methyl groups in the nucleus seems to produce an effect similar to that obtained by methylating the amino-group, although it is curious that the tetramethyldiaminophenazine about to be described should have a redder tint in spite of the absence of methyl groups in the nucleus.

3 : 7-*Tetramethyldiaminophenazine*,



This substance is described by Karrer (*Ber.*, 1916, **49**, 1643) as being formed by oxidising a mixture of dimethyl-*p*-phenylenediamine and dimethyl-*m*-phenylenediamine with potassium dichromate solution in presence of hydrochloric acid. The process was carried out as described and the phenazine compound separated in the form of the hydriodide, from which the base was precipitated by ammonia, filtered, washed, and extracted with alcohol. The residue was dissolved in dilute hydrochloric acid and the hydrochloride evaporated to dryness in a vacuum desiccator. The methochloride was prepared in the usual way (see p. 2059) by the action of methyl sulphate on the acetylated base dissolved in nitrobenzene and subsequent hydrolysis with concentrated hydrochloric acid. The colour of the methochloride dissolved in water, which closely resembles that of the hydrochloride (as is usually the case), is a violet-red, as described by Karrer. According to Karrer, the base has the formula given above.

Bamberger (*Annalen*, 1890, **257**, 1) has shown that *N*-methyltetrahydroquinoline (kairoline) has properties closely resembling those of dimethylaniline, and, like the latter, yields a nitroso-derivative. It seemed an interesting point to determine whether an azine colouring matter is produced in the same way as Toluylene-red methochloride and also to examine the colour of the product.

3-*Amino*-2-*methyl*-N-*methyltetrahydroquinolinophenazine Methochloride* (Formula XII).

The tetrahydroquinoline and its *N*-methyl derivative were prepared by the method of Hoffmann and Königs (*Ber.*, 1883, **16**, 728) and the latter was converted into the nitroso-compound (Königs and Freer, *Ber.*, 1885, **18**, 2388). A mixture of 2·6 grams of nitroso-*N*-methyltetrahydroquinoline, 1·5 grams of *p*-dimethylamino-*o*-toluidine, 15 c.c. of glacial acetic acid, and 2 c.c. of concentrated hydrochloric acid was warmed gently on the water-bath. Heat was developed and the liquid acquired a brilliant green colour which rapidly changed through brownish-black, dull scarlet, to magenta. The heating was continued for three to four hours, when the product was dissolved in 50 c.c. of hot water, filtered, and the colouring matter precipitated with zinc chloride and brine. It formed a green, iridescent mass, which was at first sticky, but rapidly hardened. The substance dissolves in water with a magenta colour similar to that of Toluylene-red methochloride. It has the formula $C_{18}H_{21}N_4Cl,HCl$ (Found: N = 14·5. $C_{36}H_{42}N_8Cl_4Zn$ requires N = 14·1 per cent.). Attempts to prepare colouring matters from the nitroso-*N*-methyltetrahydroquinoline and *m*-phenylenediamine and tolylenediamine were unsuccessful. The reaction in both cases was very violent and resulted in the formation of insoluble substances, whereas when more dilute acid was used, no colouring matter seemed to be formed.

For purposes of comparison, the following three substances were prepared. They are mentioned by Friedländer (*op. cit.*, Vol. III, p. 397) as possessing a redder shade than the preceding compounds.

3-*Amino*-7-*methylamino*-2-*methylphenazine Methochloride* (Formula VII).

The substance was prepared from nitrosomonomethylaniline hydrochloride and *o*-aminodimethyl-*p*-toluidine dissolved in alcohol according to the quantities given in D.R.-P. 80758 (Friedländer, *op. cit.*, Vol. IV, p. 376): The mixture was boiled for six hours. The scarlet colour developed in a few minutes and rapidly intensified until a precipitate began to form, when the liquid was somewhat concentrated and cooled. The precipitate was filtered and washed with a little alcohol. The phenazine compound, $C_{15}H_{17}N_4Cl,HCl$, consists of a green, crystalline powder which dissolves in water with a redder shade than the preceding compounds, and at the same time a more magenta shade than the scarlet dyes about to be described.

3-*Amino*-7-*methylamino*-2 : 8-*dimethylphenazine Methochloride* (Formula VIII).

The methyl-*o*-toluidine employed in the reaction was obtained by the usual method, namely, by heating together at 200—220° for eight hours *o*-toluidine, methyl alcohol, and hydrochloric acid. The crude base was purified by conversion into the nitrosoamine. Twenty grams were dissolved in 24 c.c. of concentrated hydrochloric acid and 60 c.c. of water, cooled to 0—5°, and 5 grams of sodium nitrite in 15 c.c. of water added slowly with stirring. A pale orange oil separated, and was extracted with ether. It yielded 10 grams of the nitrosoamine. A portion of this was reduced with stannous chloride and gave 4 grams of the pure base, b. p. 206—208°.

Another portion of the nitrosoamine in ether solution was heated (O. Fischer and Hepp, *Ber.*, 1886, **19**, 2991) with alcoholic hydrogen chloride on the water-bath and boiled gently under reflux. A white, crystalline deposit slowly formed and after about an hour the precipitation was complete. The crystalline precipitate was filtered and dried. The mother-liquor yielded a further quantity on dilution with ether.

The colouring matter was prepared in the manner described above by boiling together on the water-bath *m*-aminodimethyl-*p*-toluidine in alcohol with nitrosomonomethyl-*o*-toluidine hydrochloride and hydrochloric acid. The yellowish-red colour which first developed intensified rapidly to a much redder shade with no trace of blue, but not so yellow as Azine Scarlet G. The colouring matter partly precipitated in the boiling liquid and was separated by concentration, cooling, filtering, and washing with ether. The compound forms a powder which dissolves in water with a red colour, and has probably the formula $C_{16}H_{19}N_4Cl,HCl$.

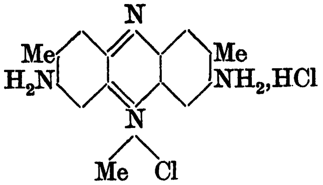
3-*Amino-7-benzylamino-2 : 8-dimethylphenazine Methochloride* (Formula IX).

The benzyl-*o*-toluidine was prepared in accordance with Fleischer's method (*Annalen*, 1866, **138**, 228) by heating together at 160° for two hours benzyl chloride (1 mol.) and *o*-toluidine (2 mols.). It boiled at 220°/16 mm. The distillate at once solidified to a colourless mass, m. p. 56—57°. The nitrosoamine described by Kohler (*Annalen*, 1887, **241**, 360) was prepared by the action of sodium nitrite on the base dissolved in dilute sulphuric acid, and melted at 53°. It was dissolved in 20 c.c. of alcoholic hydrogen chloride, and warmed on the water-bath for an hour. The brown nitroso-compound which separated on dilution with ether was used in the crude state for the preparation of the colouring matter. The *p*-dimethylamino-*o*-toluidine dissolved in alcohol with the nitroso-benzyl-*o*-toluidine hydrochloride and hydrochloric acid were heated together on the water-bath as described in the previous preparation. The colour developed, passing from yellowish-red to red with a faintly blue tint, but there was no indication of the brilliant red of Azine Scarlet G. On concentration and cooling, the colouring matter separated, and was filtered and washed with ether. The shade in aqueous solution was slightly bluer than that of the previous compound. It has probably the formula $C_{22}H_{23}N_4Cl,HCl$.

The following series consists of a group of scarlet dyestuffs, including "Azine Scarlet G," some of which are described under D.R.-P. 86608 of the Farbwerke Mühlheim (Friedländer, *op. cit.*, Vol. IV, p. 380). All these compounds contain unsubstituted amino-groups.

3 : 7-*Diamino-2 : 8-dimethylphenazine Methochloride* (Azine Scarlet G).

The quantities given in D.R.-P. 86608 (*loc. cit.*) were heated together with stirring at 110°. As the reaction proceeded, much frothing occurred, which subsided when the process was complete (about three hours). The semi-solid, crystalline product was dissolved in nearly boiling water, filtered if necessary, and hydrochloric acid added. On cooling, green, iridescent needles separated. A quantity of the colouring matter remained in the mother-liquor. The substance dissolves in water with a bright scarlet colour (Found: N = 17·5, 17·6. $C_{15}H_{18}N_4Cl_2$ requires N = 17·1 per cent.). The formula is therefore



Azine Scarlet G.

3 : 7-*Diamino*-8-*methylphenazine Methochloride* (Formula III).

The preparation was carried out under similar conditions to the above, a proportionate amount of aminoazobenzene hydrochloride being used in place of the toluene compound. The final product did not crystallise so readily, and required the addition of sodium chloride to assist precipitation. The colouring matter was recrystallised from dilute hydrochloric acid and formed green, iridescent crystals, which dissolved in water with a scarlet colour similar to that described previously (Found : N = 18·5. $C_{14}H_{15}N_4Cl,HCl$ requires N = 18·0 per cent.).

5 : 9-*Diamino*-10-*methylnaphthaphenazine Methochloride* (Formula VI).

The preparation was carried out as above, a proportionate amount of benzeneazo-α-naphthylamine hydrochloride and one and a half times the amount of glycerol being used and heating at 120° being maintained for three and a half hours. Some insoluble matter was formed, which was filtered from the hot aqueous solution. A little salt and hydrochloric acid were used to precipitate the dye. It was recrystallised from dilute hydrochloric acid, the pure product forming green, iridescent crystals. The formula is $C_{18}H_{17}N_4Cl,HCl$. In order to compare the colour of the above with aminophenazines in which one or two amino-groups were substituted for hydrogen in only one nucleus, 2-aminophenazine and 2 : 3-diaminophenazine were prepared.

2-*Aminophenazine* was prepared by the method of Wohl and Lange (*Ber.*, 1910, **43**, 2186) by heating *o*-nitroaniline and aniline hydrochloride in presence of fused zinc chloride, and also by a method of Kehrmann and Harras (*Ber.*, 1913, **46**, 431). The products in the two cases appear to be identical. It crystallises in brilliant red needles, m. p. 283°. It was converted into the acetyl derivative, from which the methochloride was obtained by the action of methyl sulphate in nitrobenzene solution (p. 2059). It forms a red, crystalline compound. Both the hydrochloride of aminophenazine and the methochloride dissolve in water with a bright magenta colour. The absence of a second amino-group in the second ring seems to produce a similar effect to methylation of the amino-group.

2 : 3-*Diaminophenazine* was obtained by the method of Ullmann and Mauther (*Ber.*, 1902, **35**, 4302). It was converted into the acetyl derivative and subsequently into the methochloride. The methochloride crystallises in black needles. Both substances dissolve with an orange or orange-red colour in different solvents. Here the presence of a second amino-group in the same nucleus produces a fundamental change in the colour of the substance.

Synopsis of the Principal Dyes of the "Azine Scarlet" Group.

Formula.	Colour in aqueous solution.	Reference.
II.	Magenta	Toluylene Red. D.R.-P. 69188. Fried., Vol. III, p. 397. S. and J., No. 582, p. 228.
I.	Magenta (bluer shade)	Witt, *Ber.*, 1879, **12**, 931. D.R.-P. 15272 (1880).
XV.	Magenta (similar to I)	D.R.-P. 69188.
XVI.	Magenta (similar to II)	"
XVII.	Magenta (similar to I)	"
XII (+ HCl).	Magenta (similar to I)	—
VIII (+ HCl).	Redder than the above	D.R.-P. 80758 (Fried., Vol. IV, p. 376).
IX (+ HCl).	Similar to VIII, but slightly bluer	"
IV (+ HCl).	Scarlet	D.R.-P. 86608. Azine Scarlet G. Fried., Vol. IV, p. 380.
III (+ HCl).	Scarlet (similar to IX)	"
V (+ HCl).	Scarlet (similar to IV)	*Ber.*, 1890, **23**, 845.
VI (+ HCl).	Scarlet (similar to IV, but less yellow)	D.R.-P. 86608.

Summary.

1. The formation of the quaternary methochloride has only a slight effect on the tint of the parent hydrochloride (I and II).

2. The transition from a simple amino-group through a mono-alkylated to a dialkylated amino-group is accompanied by a gradation in tint from pure scarlet, through scarlet magenta, to pure magenta. The heavier the radicle the bluer the shade (VIII and IX).

3. The transference of both amino-groups to the same nucleus produces a fundamental change in colour.

4. The replacement of a benzene by a naphthalene or tetrahydroquinoline nucleus produces little change in tint.
5. The absence of radicles in the nucleus enhances the blueness of the shade.

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THE UNIVERSITY, LEEDS.
[*Received, October 25th,* 1921.]

CCXXXVIII.—*The Action of Light of Short Wave-lengths on some Organic Acids and their Salts.*

By FRANS MAURITS JAEGER.

RECENTLY, while studying the velocity of the photochemical decomposition of solutions of the complex oxalate of potassium and tervalent cobalt—a salt which is highly photosensitive—the author observed that this velocity is strongly influenced by the presence of certain cations in the solution. Further examination showed that the progressive addition of neutral salts first increased the velocity in all cases to a maximum, still larger quantities of salt considerably diminished the velocity, and in some cases the photochemical reaction could even be stopped completely by adding enough of the neutral salt. The greater the electrical charge of the cation of the salt added, the smaller was the concentration of the salt required to bring about a maximum velocity of the photochemical reaction. Thus, for instance, the ferric ion brought about a maximal rate at a very small molecular concentration. It was thus that the effect of certain ions on the reactions proceeding under the influence of light radiation was observed, and the observation stimulated the author to take up again older experiments of a like nature. Several years previously he found (*Proc. Roy. Acad. Sci. Amsterdam*, 1911, **14**, 342) that an aqueous solution of trichloroacetic acid, in which freshly-precipitated colloidal ferric hydroxide had been dissolved in an amount insufficient to form a neutral salt, was rapidly decomposed by daylight or by the radiation of the mercury arc. Carbon dioxide was produced and a white, crystalline solid, pure hexachloroethane, C_2Cl_6, separated. A more detailed study showed that, in particular, the blue, the violet, and the ultra-violet rays act most intensely, in accordance with their maximal specific absorption. The mechanism of the process seemed, however, to be more complicated than was originally supposed; the reaction in dilute solutions was found to differ from that in concentrated ones. Moreover, the presence of free oxygen has an important effect, in leading to the production of free chlorine and of hydrochloric acid. Although the solutions show all the specific reactions of the free ferric ion, there is no doubt that they contain the iron as a constituent of a complex hexa-trichloroacetatoferric ion, which is, however, readily dissociated. If there is no excess of free acid in the solution, the above-mentioned photochemical action does not take place, but another is observed, analogous to the decomposition which occurs when the solution is heated, and resulting in the formation of carbon dioxide and chloroform. If a concentrated solution of trichloroacetic acid is electrolysed between platinum electrodes, the trichloromethyl ester of the acid is formed, as well as carbonyl chloride and hydrochloric acid; the trichloromethyl trichloroacetate in its turn can be split by catalysts into carbon dioxide and hexachloroethane.

It was further possible to prove that aqueous solutions of ferric tribromoacetate and pentachloropropionate are decomposed photochemically, with formation of carbon dioxide and bromoform, and of tetrachloroethylene respectively. The photochemical processes normally occurring can be expressed by the equations :

$$2Fe^{\cdot\cdot\cdot} + 2CCl_3{\cdot}CO{\cdot}O' \longrightarrow 2Fe^{\cdot\cdot} + 2CO_2 + C_2Cl_6.$$
$$Fe^{\cdot\cdot\cdot} + 3CBr_3{\cdot}CO{\cdot}O' + 3H_2O \longrightarrow Fe(OH)_3 + 3CHBr_3 + 3CO_2.$$
$$Fe^{\cdot\cdot\cdot} + 3CCl_3{\cdot}CCl_2{\cdot}CO{\cdot}O' \longrightarrow Fe^{\cdot\cdot\cdot} + 3Cl' + 3C_2Cl_4 + 3CO_2.$$

More recently, while studying the influence of light radiation on aqueous solutions of potassium tribromoacetate, it was found that the originally neutral reaction became gradually more and more acid. Added silver nitrate produced a heavy precipitate of silver bromide in increasing quantity as the exposure was prolonged. This observation, in conjunction with what has been said above, suggested a more detailed study of solutions of the potassium salts of this and other similar derivatives of acetic acid when exposed to the radiation of the mercury arc. The photochemical decompositions thus effected were found to differ widely from those observed with the free acids and with their ferric salts under corresponding conditions.

As the behaviour is most evident in the case of tribromoacetic acid, it is advisable to begin with this, as being the least complicated process. When an aqueous solution of potassium tribromoacetate in a quartz vessel is exposed to the rays of a mercury lamp, the course of the reaction depends greatly on the concentration. In dilute solutions, two molecules of hydrobromic acid are formed from each molecule of the salt, while the presence of three equivalents of ionic bromine could be ascertained by gravimetric analysis. Moreover, the colourless gas which was produced at the same time was subjected to a careful gasometric examination and proved to be an equimolecular mixture of carbon dioxide and carbon monoxide. The latter gas was identified by palladous chloride and estimated quantitatively by absorption in an ammoniacal cuprous chloride solution. The reaction can therefore be completely expressed by the equation:

$$CBr_3{\cdot}CO{\cdot}O' + K^{\cdot} + H_2O \longrightarrow 2H^{\cdot} + 3Br' + K^{\cdot} + CO + CO_2.$$

When, however, more concentrated solutions were treated in the same way, the formation of bromoform as a by-product could be demonstrated,, whilst rather less bromine was found on addition of silver nitrate and a smaller quantity of free acid was produced. Evidently a secondary reaction goes on here, which in the case of the pure acid alone would be represented by the equation:

$$CBr_3{\cdot}CO{\cdot}O' + H^{\cdot} \longrightarrow CHBr_3 + CO_2.$$

On the other hand, if the ferric salt, in the presence of an excess of free acid, was exposed to the mercury light, the reaction went on in a manner quite analogous to that of ferric trichloroacetate, and resulted in the formation of hexabromoethane and carbon dioxide. The complete set of reactions observed may be expressed by the equations:

$$2CBr_3{\cdot}CO{\cdot}O' + 2Fe^{\cdot\cdot\cdot} \longrightarrow C_2Br_6 + 2CO_2 + 2Fe^{\cdot\cdot} \quad . \quad . \quad . \quad . \quad (1)$$

$$CBr_3{\cdot}CO{\cdot}O' + H^{\cdot} \longrightarrow CHBr_3 + CO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$CBr_3{\cdot}CO{\cdot}O' + K^{\cdot} + H_2O \longrightarrow 2H^{\cdot} + 3Br' + K^{\cdot} + CO + CO_2 \quad (3)$$

Reaction (2) is an occasional, secondary one. The particular way in which the tribromoacetic ion is decomposed photochemically is therefore evidently very dependent on the presence of special ions in the solution. With ferric ions present, the reaction velocity in this and in other cases is generally much greater than when hydrogen or potassium ions are present. It is not hazardous to suppose that this acceleration is in some way connected with the multiple electrical charge of the ferric ion and the relative facility with which one of the three charges is eventually removed from it.

The reaction produced under the same conditions in a solution of potassium trichloroacetate was found to be of a much more complicated character, the result being evidently a superposition of several different processes, all depending on the prevalence of certain conditions. If the solution of the potassium salt is very concentrated, only an exceedingly small amount of carbon dioxide is generated, and the gas evolved consists almost entirely of carbon monoxide, whilst, at first, for each molecule of carbon monoxide two ions of chlorine seem to be produced. With more prolonged exposures, however, the ratio of chlorine ions to carbon monoxide gradually falls off, and chloral could be detected in the liquid; the falling off of the ratio is doubtless connected with the probable presence of some free oxygen in the gaseous mixture liberated. In the presence of water and the absence of oxygen, chloral is totally destroyed by light radiation according to the equation $CCl_3{\cdot}CHO + H_2O \longrightarrow 3HCl + 2CO$, whilst, with oxygen present, the carbon monoxide is partly oxidised to carbon dioxide, and the hydrochloric acid even to chlorine. Although no final equations can be given here for the individual reactions taking place, but only preliminary ones, a general review of all the experimental data obtained may be of use for the purpose of comparison:

$$CCl_3{\cdot}CO{\cdot}O' + H^{\cdot} \longrightarrow CHCl_3 + CO_2$$

with $CHCl_3 + 3H_2O \longrightarrow 4H^{\cdot} + 3Cl' + H{\cdot}CO{\cdot}O'$

$$2CCl_3{\cdot}CO{\cdot}O' + 2Fe^{\cdot\cdot\cdot} \longrightarrow C_2Cl_6 + 2CO_2 + 2Fe^{\cdot\cdot}$$

$$CCl_3{\cdot}CO{\cdot}O' + K^{\cdot} + H_2O \longrightarrow CCl_3{\cdot}CHO + K^{\cdot} + OH' + O$$

with $CCl_3{\cdot}CHO + H_2O + 2O \longrightarrow 3H^{\cdot} + 3Cl' + 2CO_2$

(Schoorl and Van den Berg, *Chem. Zentr.*, 1906, i, 441, 650) and $CCl_3{\cdot}CHO + H_2O \longrightarrow 3H^{\cdot} + 3Cl' + 2CO$, at the same time. Depending on the presence of certain other ions in the exposed liquid, the decomposition by the action of light can thus proceed in at least three principal ways, not counting the subsidiary reactions. These reactions differ from those induced by electrolysis or by heat. The electrolytic decomposition is:

$$3CCl_3{\cdot}CO{\cdot}O' + 3H^{\cdot} + H_2O \longrightarrow CCl_3{\cdot}CO{\cdot}O{\cdot}CCl_3 + 2CO_2 + COCl_2 + Cl' + H^{\cdot}$$

and, with catalysts, eventually $CCl_3{\cdot}CO{\cdot}O{\cdot}CCl_3 \longrightarrow CO_2 + C_2Cl_6$. The thermal decomposition is:

$$CCl_3{\cdot}CO{\cdot}O' + K^{\cdot} + H_2O \longrightarrow CHCl_3 + HCO_3' + K^{\cdot}$$

The photochemical decomposition of mono- and di-chloroacetic acids has already been studied by Benrath (*Annalen*, 1911, **382**, 222) and by Euler and Cassel (*Zeitsch. physikal. Chem.*, 1913, **84**, 371). The reaction proceeds according to the schemes:

$$CH_2Cl{\cdot}CO{\cdot}O' + H_2O \longrightarrow CH_2(OH){\cdot}CO{\cdot}O' + H^{\cdot} + Cl'$$

and $CHCl_2{\cdot}CO{\cdot}O' + 2H_2O \longrightarrow CH(OH)_2{\cdot}CO{\cdot}O' + 2H^{\cdot} + 2Cl'$

These reactions are of some interest in connexion with the behaviour of the potassium salt of *trichlorolactic acid*, $CCl_3{\cdot}CH(OH){\cdot}CO{\cdot}OH$, when exposed to mercury rays. In that case, evidently only an insignificant quantity of free acid is generated, but for each molecule of the potassium salt 1 molecule of carbon dioxide is set free and one equivalent of chlorine is found to be present as ion. If the solution after exposure is feebly acidified with acetic acid and heated with semicarbazide hydrochloride, a yellow, crystalline product is obtained, which proves to be the disemicarbazone of glyoxal. According to Harries and Temme (*Ber.*, 1909, **40**, 171) and to Kling (*Bull. Soc. chim.*, 1909, [iv], **5**, 412), this fact indicates the original presence of dichloroacetaldehyde, which by a secondary reaction is transformed to glyoxal hydrate when heated with a feebly acid solution of semicarbazide. The photochemical reaction can therefore be represented by the equation:

$$CCl_3{\cdot}CH(OH){\cdot}CO{\cdot}O' + K^{\cdot} \longrightarrow CO_2 + CHCl_2{\cdot}CHO + Cl' + K^{\cdot} \quad (4)$$

whilst the secondary, purely chemical change occurs as follows:

$$CHCl_2{\cdot}CHO + 2H_2O \longrightarrow CH(OH)_2{\cdot}CHO + 2Cl' + 2H^{\cdot}$$

It may be remarked that the photochemical transformation is in this case accompanied, or immediately followed, by an intramolecular rearrangement of the atoms, and that the photochemical process does not differ here from the thermal decomposition, for aqueous solutions of the potassium salt are likewise decomposed on heating according to equation (4) above.

In continuation of the above experiments, the photochemical decomposition of triphenylacetic acid has been studied in some detail. Both the acid and its potassium salt are only sparingly soluble, and therefore solutions in alcohol–water mixtures of various concentrations were employed. In dilute solutions, the photochemical reaction rapidly results in the liberation of carbon dioxide, which dissolves in the liquid, and in the production of a white, crystalline solid, which after recrystallisation proves to be pure triphenylmethane (m. p. 93°), whilst the solution gradually becomes alkaline:

$$(C_6H_5)_3C{\cdot}CO{\cdot}O' + K^{\cdot} + H_2O \longrightarrow (C_6H_5)_3CH + HCO_3' + K^{\cdot}$$

In more concentrated solutions, an additional change takes place and a crystalline mixture is deposited which for the most part consists of triphenylcarbinol (m. p. 163°), dissolving in concentrated sulphuric acid with a yellow colour. This second photochemical process evidently occurs according to the scheme:

$$(C_6H_5)_3C{\cdot}CO{\cdot}O' + K^{\cdot} + H_2O \longrightarrow (C_6H_5)_3C{\cdot}OH + K^{\cdot} + H{\cdot}CO{\cdot}O'$$

whilst the formate produced is partly decomposed.

In analogous circumstances, phenylbromoacetic acid, as potassium salt, is readily decomposed without liberation of carbon dioxide. In the liquid, a considerable amount of ionic bromine could be demonstrated. On closer examination, it could be shown that for each molecule of the salt one equivalent of bromine is precipitated as silver bromide, whilst the characteristic odour of benzaldehyde is noticed. Evidently the original photochemical process consists in the formation of mandelic acid, which in its turn is split into benzaldehyde and formic acid. Since the solutions were stirred by a current of air, so that free oxygen was present, the secondary reactions are partly also those studied by Berthelot and Gaudechon (*Compt. rend.*, 1910, **150**, 1690; **151**, 1349; 1911, **152**, 262; **153**, 383; 1913, **157**, 333) in the case of mandelic acid, and by Benrath (*Annalen*, 1911, **382**, 222; *J. pr. Chem.*, 1917, [ii], **204**, 190) and Ciamician and Silber (*Ber.*, 1913, **46**, 1558) in the case of formic acid, when exposed to such radiation under the same conditions. In its principal features, the sequence of reactions occurring here may be represented thus:

$$C_6H_5\cdot CHBr\cdot CO\cdot O' + K^{\cdot} + H_2O \longrightarrow C_6H_5\cdot CH(OH)\cdot CO\cdot O' + Br' + H^{\cdot} + K^{\cdot}$$

and $$C_6H_5\cdot CH(OH)\cdot CO\cdot O' + H^{\cdot} \longrightarrow C_6H_5\cdot CHO + CO_2 + H_2.$$

Finally, some preliminary experiments were made with the yellowish-green ferric complex salt of ethyltartronic acid, or rather with the potassium salt of the complex ferrictri(ethyltartronic) ion, the solution of which is very sensitive to the action of light. The green solution became colourless, carbon dioxide was produced, and the liquid reduced silver nitrate solution immediately with formation of finely-divided, black, metallic silver. On keeping or passing oxygen into it, the colourless solution gradually resumes a green colour and then the original salt can be precipitated by alcohol. Evidently the photochemical reaction in this case is completely analogous to the well-known photochemical reduction of potassium ferric oxalate to potassium ferrous oxalate. The latter salt is also a very effective reducing agent for silver salts, and is easily reoxidised by free oxygen to the original ferric salt. If this be so—and by further investigation the author hopes to confirm this—the photochemical process (5) and the subsequent oxidation may probably be represented by the equations:

$$2[Fe\{OH\cdot CEt(CO\cdot O)_2\}_3]''' + 2H_2O \longrightarrow 2[Fe\{OH\cdot CEt(CO\cdot O)_2\}_2]'' + 2HCO_3' + 2CO_2 \text{ and } + \underset{\gamma\delta\text{-hexylene glycol (?)}}{OH\cdot CHEt\cdot CHEt\cdot OH} \quad . \; . \; . \; . \quad (5)$$

$$6[Fe\{OH\cdot CEt(CO\cdot O)_2\}_2]'' + 3O \longrightarrow 4[Fe\{OH\cdot CEt(CO\cdot O)_2\}_3]''' + Fe_2O_3.$$

One product of the first reaction has an agreeable aromatic odour, reminiscent of celery leaves, but its identity can be established only by further experiment.

We may state, in conclusion, by way of summary, that the various photochemical reactions of the substances dealt with are in each case truly specific, and are directly comparable neither to the effects of electrolysis nor, in most cases, to those of heat. Both electrolytic and thermal effects have occasionally been considered analogous to photochemical change. The above and other experiments enable us to emphasise once more that in the case of photochemical change no such general comparisons are valid; each photochemical reaction is specific and very dependent on the conditions obtaining at the moment, so that it is scarcely ever possible to predict its course. Among the conditions governing the reaction, the presence of certain ions in the solution must be considered a factor of great importance.

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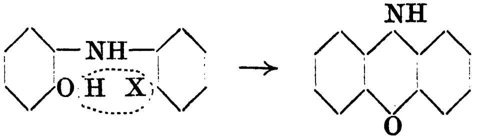
CCXXXIX.—*A New Synthesis of Oxazines.*

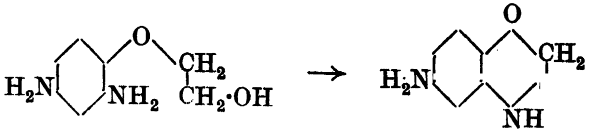
By ARTHUR FAIRBOURNE and HAROLD TOMS.

SYNTHESES of oxazines are usually brought about by the preliminary formation of a nitrogen linking, followed by the completion of an oxazine ring, according to the following scheme:



This has the disadvantage, however, of affording no simple method of preparation of amino-derivatives, the reduction of nitro-oxazines being by no means easy; and it otherwise very greatly limits the type of substance obtainable.

Research now in progress (compare the previous paper, this vol., p. 1036) has resulted in a different formation of oxazines, which is the converse of the usual process, that is, it consists in the closing of a simple ether chain by the elimination of water from an amino- and a hydroxyl-group:



The oxazines being of very considerable interest, both technically (compare Justin-Mueller, *Rev. Gen. Col.*, 1920, **24**, 130; also, in connexion with amino-derivatives, Kehrmann, *Ber.*, 1905, **36**, 481, 483) and, more especially, scientifically (compare Knorr, *Ber.*, 1899, **22**, 1209; Kehrmann, *loc. cit.*, p. 479), this alternative and rather unexpected possibility of their synthesis appears sufficiently useful to be put on record, the only previous example of a preparation in any way similar which has come to the notice of the authors being a condensation of amino- and carboxyl-groups (Bischoff, *Ber.*, 1900, **33**, 1593), the carbonyl of the latter remaining in the ring produced, and not readily allowing of reduction to the parent oxazine.

EXPERIMENTAL.

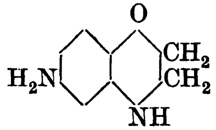
2 : 4-*Dinitrophenyl* β-*Hydroxyethyl Ether, and its Reduction.*

This substance was prepared by a method similar to that employed in the case of the corresponding ether of glycerol (*loc. cit.*), a small quantity of aqueous sodium hydroxide solution proving successful, however, as condensing agent instead of the sodium derivative of ethylene glycol. To a solution of 8·1 grams of 1-chloro-2 : 4-dinitrobenzene in 18 c.c. of ethylene glycol was added an ethylene-glycollic solution of sodium hydroxide (1 mol.) obtained by dissolving 1·6 grams of the solid alkali in 1 c.c. of water and adding 18 c.c. of the glycol. The mixture was heated on a water-bath for half an hour, during which time crystals of sodium chloride separated. While still hot, the liquid was stirred into 50 c.c. of water, from which, on cooling, were deposited 8·5 grams of acicular crystals. These were recrystallised from 20 per cent. acetic acid and from water, and were then colourless and melted at 109° (Found: C = 42·15; H = 3·75; N = 12·47. Calc., C = 42·11; H = 3·51; N = 12·29 per cent.).

The mother-liquor from the acetic acid crystallisation contained a small quantity of another substance, m. p. 192—195°, which was not sufficient to admit of complete analysis, but an estimation of the nitrogen indicated that the compound was ethylene glycol bisdinitrophenyl ether, $C_2H_4(O{\cdot}C_6H_3[NO_2]_2)_2$. In other experiments, the ethylene-glycollic sodium hydroxide was prepared by pouring the strong aqueous alkali into the glycol, instead of pouring the glycol into the aqueous alkali, and in the subsequent condensations with chlorodinitrobenzene no trace of the bisdinitrophenyl ether could then be found. It would consequently appear that the presence of excess of the glycol during the whole period of the preparation of the glycollic alkali prevented the formation of the disodium derivative of glycol, and consequently of the bisdinitrophenyl ether also.

Reduction of 2 : 4-*Dinitrophenyl* β-*Hydroxyethyl Ether.*—One part by weight of the monophenyl ether was gradually added to twenty-two parts of water containing two parts of iron and a small quantity of hydrochloric acid, the addition being extended over a quarter of an hour, and being carried out at 74—76°. The whole was maintained at this temperature for a further equal period of time, the product was then filtered and the residue extracted with boiling water. As the resulting diamine was found to be insoluble in ether, and exceedingly difficult to purify in any form, the water was evaporated and the dried material was submitted to dehydration in the crude state, as described below. No specimen of this free diamine has been isolated, but, by boiling the crude product with excess of acetyl chloride and then decanting and diluting the solution obtained, long, colourless needles of the triacetyl derivative were isolated, m. p. 128—130° (Found: $CH_3{\cdot}CO = 43{\cdot}1$. Calc., $CH_3{\cdot}CO = 43{\cdot}8$ per cent.).

6-*Amino*-2 : 3-*dihydro*-1 : 4-*benzisooxazine* (6-*Aminobenzomorphine*),



The crude diamine mentioned above was dissolved in 10 parts by weight of concentrated sulphuric acid, and heated slowly to 150°, at which temperature it was maintained for several minutes. The product was cooled, poured into water, and extracted with ether after neutralisation with sodium hydroxide. The ethereal extract was dried over solid sodium hydroxide, and the ether was removed by evaporation, when a mass of colourless, acicular crystals was obtained, which, after recrystallisation from water, melted at 80° (Found: N = 18·9. Calc., N = 18·6 per cent.).

The authors wish to express their indebtedness to the Chemical Society for a grant to one of them (H. T.) which has partly defrayed expenses incurred in this work.

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CCXL.—*The Influence of Neutral Salts on the Hydrolysis of Ethyl Formate.*

By Alexander Bernard Manning.

Neutral salt action, as ordinarily measured, is probably due to two or more causes acting together, and the difficulty in explaining the total effect in any particular example lies in disentangling these causes and assigning to each its specific effect.

If to a solution of an electrolyte HA we add a neutral salt BC, there will be in general a change in the concentration of the ion $H^{\cdot}$ owing to the formation of the new molecular species HC and BA and the consequent readjustment of the concentrations of the ions present. The change in concentration of $H^{\cdot}$ due to this cause may be called the *true* neutral salt action.

Of other effects often included under neutral salt action the most prominent is due probably to *hydration* and the consequent changes in concentration of the solvent. To quote one instance—it is known that the presence of potassium chloride increases the rate at which sucrose is hydrolysed by an acid, but a comparable increase in velocity of hydrolysis can be produced also by the presence of a neutral non-electrolyte, for example, mannitol (Rosanoff and Potter, *J. Amer. Chem. Soc.*, 1913, **35**, 248), or indeed sucrose itself, for the rate of hydrolysis increases considerably with initial concentration of sugar. In all investigations on neutral salt action an attempt should be made to estimate the hydration factor by a careful comparison of the effect of addition of the neutral salt with that of the addition of some otherwise inactive non-electrolyte, the hydration effect of which has been otherwise determined. This was done in the work described below, and by a fortunate chance it was found that the method chosen was practically independent of hydration effects, glucose and sucrose even in considerable concentrations producing inappreciable changes in the particular reaction constant measured. On the assumption that there are no other disturbing influences, the following experimental work should give a measure of the true neutral salt action as defined above. The results will be discussed from this point of view.

EXPERIMENTAL.

Dilute aqueous solutions of ethyl formate (1—2 per cent.) hydrolyse at a conveniently measurable rate at 25°, in the absence of acid other than that produced by the hydrolysis. The course of this reaction in water alone and in solutions of various neutral salts and non-electrolytes has been studied. The reaction

$$H{\cdot}CO_2{\cdot}C_2H_5 + H_2O \longrightarrow H{\cdot}CO_2H + C_2H_5{\cdot}OH$$

is autocatalytic and for dilute solutions of the ester can be taken as complete.

To obtain an expression for the course of the change it will be assumed, as a working hypothesis, that the rate of hydrolysis is jointly proportional to the concentration of the ester and of the hydrion.

Let a = the initial concentration of ester.
x = the concentration of formic acid produced after time t.
c = the concentration of undissociated formic acid at time t.
c_1 = concentration of hydrion at time t.

Then $$c + c_1 = x \qquad (1)$$

And $$\frac{c_1^2}{c} = k_1, \text{ the ionisation constant of formic acid at } 25° \qquad (2)$$

The above assumption gives

$$\frac{dx}{dt} = K(a - x)c_1 \qquad (3)$$

We may call K the *reaction constant.*

Eliminating c and c_1 from (1), (2), and (3), we have

$$\frac{dx}{dt} = \tfrac{1}{2}Kk_1(a - x)\left\{\sqrt{1 + \frac{4x}{k_1}} - 1\right\}.$$

This gives on integration

$$\Big[_{x_0}^{x_1} 2\log\{\sqrt{1 + k'x} - 1\} + (\sqrt{1 + k'a} - 1)\log\{\sqrt{1 + k'a} + \sqrt{1 + k'x}\} - (\sqrt{1 + k'a} + 1)\log\{\sqrt{1 + k'a} - \sqrt{1 + k'x}\}\Big]$$
$$= 2aK(t_1 - t_0), \text{ where } k' = \frac{4}{k_1} \qquad (4)$$

Initially the hydroxyl ions of the water also catalyse the reaction, but with increasing concentration of the hydrogen ions that of the hydroxyl ions soon becomes inappreciable. This initial effect is readily seen to be negligible in the present case.

The reaction was followed by titration with *N*/20-ammonia, with methyl-red as indicator. The use of a stronger alkali, such as baryta, was found to be inadmissible, since it appeared to catalyse the reaction appreciably during the titration, particularly during the early part of the reaction. This suspicion was confirmed by following the reaction (*a*) using baryta, (*b*) using ammonia, (*c*) by the electrical conductivity method. (*a*) invariably gave higher values for the amount of hydrolysis than (*b*) or (*c*) except towards the end of the reaction. The values from (*b*) and (*c*) agreed within the limits of the experimental error.

The ethyl formate used was carefully purified and was freshly distilled immediately before each series of experiments. A litre of water, or of the solution to be used, was placed in a stoppered Jena glass bottle in a thermostat at 25° ± 0·05°. When this had attained the temperature of the bath, the requisite amount of ester was pipetted into it, the bottle shaken thoroughly, and the time taken. At convenient intervals 25 c.c. of the solution were removed and titrated with the standard ammonia. The initial concentration of ester was determined exactly by adding excess of bartya to 25 c.c. of the solution, keeping for two days, and titrating the excess of baryta with hydrochloric acid, care being taken to exclude carbon dioxide.

All the salts used were recrystallised at least once. Conductivity water was used throughout for the solutions.

When using a solution of a salt or non-electrolyte, a correction was made for the alteration in concentration of the solution due to the small change in volume on addition of the ester.

The Rate of Reaction with Water alone.

Initial concentration of the ester $0{\cdot}0578M$.			Initial concentration of the ester $0{\cdot}1163M$.			Initial concentration of the ester $0{\cdot}1745M$.		
Time in hours.	Amount changed per cent.	*K*.	Time in hours.	Amount changed per cent.	*K*.	Time in hours.	Amount changed per cent.	*K*.
2·97	0·64	—	2·77	1·04	—	6·72	5·90	—
22·97	15·3	4·81	5·42	2·70	4·88	24·02	43·95	4·73
25·3	18·0	4·78	22·5	29·32	4·81	28·42	54·5	4·76
29·85	24·15	4·81	24·93	34·4	4·82	30·62	59·25	4·79
46·87	48·1	4·82	27·37	39·3	4·82	48·35	85·3	4·79
53·45	56·5	4·81	30·08	44·9	4·83	55·17	90·3	4·79
70·62	74·5	4·84	46·50	72·4	4·85	72·25	96·6	4·72
72·93	76·4	4·84	49·07	75·6	4·85	78·73	97·9	4·79
			54·03	80·9	4·86			
			70·58	91·7	4·85			
Mean *K* = 4·82			Mean *K* = 4·84			Mean *K* = 4·77		

The constancy of the calculated values of *K* fully justifies the assumptions made in deducing equation (4).

In the experiments in presence of neutral salts or non-electrolytes, the concentration of ester used was in the region of $0{\cdot}116M$. The average of several determinations of *K* for water alone and for concentrations of ester between $0{\cdot}115M$ and $0{\cdot}117M$ was 4·83. This will be taken as the basis for comparison with the values obtained in the presence of other substances.

The Rate of Reaction in Solutions of Non-electrolytes.

Glucose was the non-electrolyte principally studied; the following are typical results.

M/4-Glucose.
Conc. of the ester = 0·1163*M*.

Time in hours.	Amount changed per cent.	*K*.
4·23	1·50	–
6·87	3·43	4·
8·83	5·41	4·
23·38	30·46	4·
25·73	35·55	4·
28·30	40·76	4·
33·12	50·63	4·
47·83	74·13	4·
52·50	79·32	4·
56·57	83·3	4·
73·37	93·0	4·
97·67	97·9	4·

Mean *K* = 4·89

2*M*-Glucose.
Conc. of the ester = 0·1160*M*.

Time in hours.	Amount changed per cent.	*K*.
3·47	0·83	—
22·93	28·02	4·85
25·38	33·5	4·90
29·73	43·2	4·96
46·53	73·3	5·06
52·2	79·6	5·04
71·4	91·7	4·90

Mean *K* = 4·95

In *M*/10-glucose, the mean *K* = 4·84; and in *M*-glucose, the mean *K* = 4·92.

There appears to be a very slight, gradual increase in *K* with increasing concentration of glucose, but, as will be seen later, it is very small compared with the increase in the presence of neutral salts.

Similar results are obtained with solutions of sucrose. Thus in

M/2-sucrose, the mean *K* = 4·92.
M-sucrose, the mean *K* = 5·10.

The Rate of Reaction in Solutions of Neutral Salts.

Typical results in solutions of potassium chloride.

Conc. of KCl = 0·0993*N*.
Initial conc. of the ester = 0·1165*N*.

Time in hours.	Amount changed per cent.	*K*.
5·78	3·47	—
22·56	37·9	5·78
25·65	45·0	5·77
29·52	54·0	5·79
46·73	82·3	5·85
51·43	86·7	5·85
53·63	88·8	5·92
71·5	96·5	5·93
78·2	97·7	5·94

Mean *K* = 5·85

Conc. of KCl = 0·495*N*.
Initial conc. of the ester = 0·1165*N*.

Time in hours.	Amount changed per cent.	*K*.
4·08	2·72	—
6·08	5·25	6·52
8·08	8·54	6·45
22·5	45·5	6·53
27·27	57·7	6·54
29·33	62·4	6·54
46·93	88·0	6·55
49·38	89·7	6·52

Mean *K* = 6·52

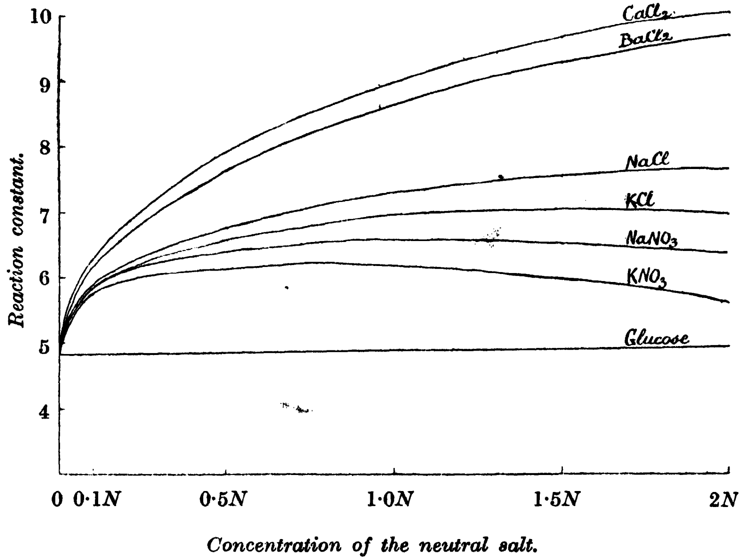
Conc. of KCl = 1·99*N*.
Initial conc. of the ester = 0·1158*N*.

Time in hours.	Amount changed per cent.	*K*.
1·73	1·22	—
6·53	7·31	6·82
23·03	52·1	6·96
25·72	58·8	6·95
30·5	69·6	6·98
47·23	90·7	6·97
49·68	92·1	6·93
71·10	98·4	6·87

Mean *K* = 6·93

The results similarly obtained with solutions of sodium chloride, potassium nitrate, sodium nitrate, calcium chloride, and barium chloride are tabulated below and represented graphically in Fig. 1.

FIG. 1.



Values of K *for Various Salts.*

Conc. of salt.	KCl.	NaCl.	KNO_3.	$NaNO_3$.	$CaCl_2$.	$BaCl_2$.
N/10	5·85	5·89	5·76	5·87	6·23	6·15
N/4 ..	6·18	—	6·01	6·17	—	6·81
N/2 ..	6·53	6·75	6·14	—	7·90	7·61
N ..	6·94	7·28	6·15	6·53	8·95	8·63
2*N* ..	6·93	7·62	5·54	6·38	10·0	9·65

In all the solutions of these salts the constancy of the values of *K*, calculated throughout the course of the reaction, was very satisfactory. Moreover, the result of addition of the salt was always to accelerate the reaction. Solutions of the sulphates behave differently. Potassium and sodium sulphates retard the reaction, and show a gradual increase in *K* as the reaction proceeds.

Below are results for potassium sulphate :

Conc. of K_2SO_4 = 0·0991N.
Initial conc. of the ester = 0·1163N.

Time in hours.	Amount changed per cent.	*K*.
3·43	1·04	—
4·95	1·56	3·22
6·03	2·18	3·69
22·92	23·4	4·14
25·35	27·65	4·15
29·67	35·75	4·19
46·47	63·9	4·26
52·15	71·3	4·27
71·37	87·5	4·28
95·7	96·1	4·30

Mean *K* = 4·06

Conc. of K_2SO_4 = 0·992N.
Initial conc. of the ester = 0·1163N.

Time in hours.	Amount changed per cent.	*K*.
2·52	0·94	—
5·13	1·77	3·00
7·98	3·22	3·17
22·0	18·6	3·58
24·47	22·45	3·63
28·83	29·6	3·68
45·63	57·3	3·82
51·6	65·2	3·84
70·53	83·6	3·90
94·37	93·8	3·88

Mean *K* = 3·61

Sodium sulphate gives similar results.

Discussion of Results.

It has been shown that solutions of glucose and sucrose of relatively high concentrations give very nearly the same values for the reaction constant *K* as does water alone. Unless, therefore, in solutions of these non-electrolytes there are two or more effects exactly annulling each other, which is improbable, it may be concluded that the rate of reaction is independent of changes in the concentration of the water. In other words, hydration of the solute does not affect *K*.

It may further be remarked that changes of viscosity have here little effect on the rate of reaction.

Admitting no further hypothesis, we must take the change in *K* on addition of neutral salts as due to an actual change in the concentration of hydrogen ions in the solution, *K* indeed giving a measure of the change. This change is a result of the readjustment in concentrations on addition of the neutral salt (say, potassium chloride) conditioned by the equilibria :

$$\begin{array}{lcl} H{\cdot}CO_2H & \rightleftarrows & H{\cdot}CO_2' + H^{\cdot} \\ KCl & \rightleftarrows & K^{\cdot} + Cl' \\ HCl & \rightleftarrows & H^{\cdot} + Cl' \\ H{\cdot}CO_2K & \rightleftarrows & H{\cdot}CO_2' + K^{\cdot} \end{array}$$

It remains to be seen whether the theory of such mixtures of electrolytes, as far as it has been developed up to the present, will lead to the same results as those obtained experimentally.

Of the four equations above, three represent the dissociation of strong electrolytes. For dealing with such mixed electrolytes as these Arrhenius (*Zeitsch. physikal. Chem.*, 1899, **31**, 197; compare also Sherrill, *J. Amer. Chem. Soc.*, 1910, **32**, 741) proposed the following form of " dilution law " :

$$\frac{\mathrm{B}^{\cdot} \times \mathrm{A}'}{\mathrm{BA}} = D(\Sigma i)^m,$$

where BA is one of the electrolytes, dissociating into the ions $\mathrm{B}^{\cdot}$ and A', Σi is the sum of the ionic concentrations, that is, the total concentration of positive (or negative) ions in the solution, and D and m are constants.

Following the method proposed by Arrhenius, the concentrations of hydrogen ion in various mixtures of potassium chloride, sodium chloride, barium chloride, and potassium sulphate respectively with formic acid have been calculated. There is, however, another point to be considered in comparing the calculated with the experimental results. During the reaction the concentration of formic acid varies, increasing from zero to slightly more than $0{\cdot}1N$. The fact that a constant value is obtained for K throughout the reaction (except for the sulphates) shows that for the same concentration of neutral salt the same proportional increase in hydrogen-ion concentration is produced, independently of the concentration of acid.

As an example, consider a solution containing $0{\cdot}1N$-formic acid in the presence of N-potassium chloride. In $0{\cdot}1N$-formic acid alone the concentration of hydrogen-ion is 0·00452 gram-ion per litre. In the mixed solution the concentrations of the various ions and molecules present are given by the following simultaneous equations :

$$\frac{\mathrm{K}^{\cdot} \times \mathrm{Cl}'}{\mathrm{KCl}} = K_1(\mathrm{K}^{\cdot} + \mathrm{H}^{\cdot})^{m_1}$$

$$\frac{\mathrm{H}^{\cdot} \times \mathrm{Cl}'}{\mathrm{HCl}} = K_2(\mathrm{K}^{\cdot} + \mathrm{H}^{\cdot})^{m_2}$$

$$\frac{\mathrm{K}^{\cdot} \times \mathrm{H{\cdot}CO_2}'}{\mathrm{H{\cdot}CO_2K}} = K_3(\mathrm{K}^{\cdot} + \mathrm{H}^{\cdot})^{m_3}$$

$$\frac{\mathrm{H}^{\cdot} \times \mathrm{H{\cdot}CO_2}'}{\mathrm{H{\cdot}CO_2H}} = K_4(\mathrm{K}^{\cdot} + \mathrm{H}^{\cdot})^{m_4}$$

$$\mathrm{K}^{\cdot} + \mathrm{KCl} + \mathrm{H{\cdot}CO_2K} = 1$$
$$\mathrm{Cl}' + \mathrm{KCl} + \mathrm{HCl} = 1$$
$$\mathrm{H}^{\cdot} + \mathrm{HCl} + \mathrm{H{\cdot}CO_2H} = 0{\cdot}1$$
$$\mathrm{HCO_2}' + \mathrm{H{\cdot}CO_2H} + \mathrm{H{\cdot}CO_2K} = 0{\cdot}1.$$

The values of the constants, found from the conductivity data, assuming the conductivity–viscosity ratio to give the degree of dissociation, are

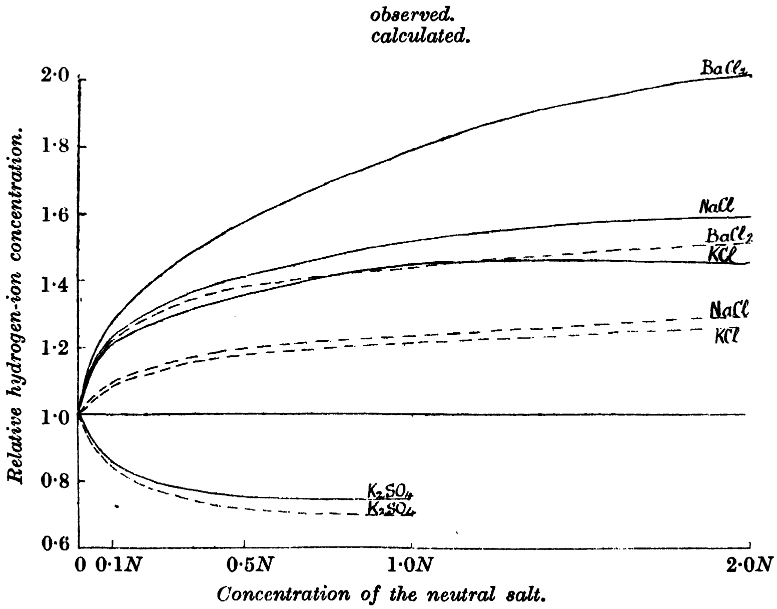
$$K_1 = 2{\cdot}44;\ K_2 = 5{\cdot}25;\ K_3 = 1{\cdot}15;\ K_4 = 0{\cdot}000214.$$
$$m_1 = 0{\cdot}62;\ m_2 = 0{\cdot}62;\ m_3 = 0{\cdot}54;\ m_4 = 0.$$

Solving the equations, we have

$H^{\cdot} = 0{\cdot}00547$ $K^{\cdot} = 0{\cdot}731$
$HCO_2' = 0{\cdot}00366$ $Cl' = 0{\cdot}733$
$KCl = 0{\cdot}266$ $H{\cdot}CO_2H = 0{\cdot}0936$
$HCl = 0{\cdot}000924$ $H{\cdot}CO_2K = 0{\cdot}00274$

Thus the addition of the neutral salt has increased the hydrogen-ion concentration from 0·00452 to 0·00547 gram-ion per litre. The increase is 21·0 per cent. The same percentage increase is produced with smaller initial concentrations of formic acid. Thus in 0·05*N*-formic acid the hydrogen-ion concentration is 0·003165 gram-ion per litre. In the presence of *N*-potassium chloride this becomes 0·00383 gram-ion per litre. The increase again is 21·0 per cent.

FIG. 2.



In the diagram (Fig. 2) is shown the calculated percentage increase in concentration of hydrogen ion in the presence of various concentrations of potassium, sodium, and barium chlorides and potassium sulphate respectively. The observed values also are shown, drawn to the same scale.

Calculation of the hydrogen-ion concentration in mixtures of potassium sulphate and formic acid shows a decrease on addition of the neutral salt. Thus:

H-ion conc. in 0·1N-formic acid .	0·00452 gram-ion per litre.
H-ion conc. in 0·1N-formic acid in presence of 0·1N-K_2SO_4 .	0·00381 ,, ,,
H-ion conc. in 0·1N-formic acid in presence of N-K_2SO_4 . .	0·00325 ,, ,,

Moreover, the decrease is not quite proportional to the original hydrogen-ion concentration. Thus in presence of N-potassium sulphate the hydrogen-ion concentration of 0·1N-formic acid decreases to 72 per cent., that of 0·05N-formic acid to 71 per cent., and that of 0·01N-formic acid to 67 per cent. of the original. Some variation in the value of K, then, is to be expected.

With the sulphates the agreement of calculated and experimental results is good. With the chlorides, however, the observed values are considerably greater than the calculated. It is true that some of the data used in the derivation of the constants in Arrhenius's formula are not very trustworthy. This applies particularly to the conductivity data for the formates in aqueous solution at 25°, which need redetermining. But the results indicate that some modification of Arrhenius's mixture law is necessary. Again, it may be noted that the nitrates show clearly, and potassium chloride gives some indication of, a maximum neutral salt effect with increasing concentration. The method of calculation used above would give no maximum. It would, however, seem useless to test any other mixture law until more trustworthy data are available for the dissociation of the formates in solution.

[NOTE.—The work described above was begun in 1914, but, very shortly after its commencement, had to be postponed until 1919. Later, it had again to be put aside, and as, at the moment, circumstances do not permit its continuation, it is being published in its present, somewhat incomplete, form.]

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CCXLI.—*The Action of Diazo-salts on Aromatic Sulphonamides. Part I.*

By Pavitra Kumar Dutt, Hugh Robinson Whitehead, and Arthur Wormall.

Hinsberg (*Ber.*, 1894, **27**, 598), by the action of benzenediazonium chloride on benzenesulphonamide in very dilute alkaline solution, obtained a yellow, crystalline product, which in the crude state melted at 102° with decomposition and on analysis gave 15·63 per cent. of nitrogen. From this, the author assigned to it the structure $SO_2Ph{\cdot}NH{\cdot}N{:}NPh$, which requires 16·09 per cent. of nitrogen. On warming with dilute acids or alkalis, it decomposed into benzenesulphonamide, phenol, nitrogen, and a resinous product.

In repeating Hinsberg's reaction with molecular quantities of *p*-toluenesulphonamide and benzenediazonium chloride, we obtained a yellow, crystalline product which, however, smelt strongly of phenylazoimide. On recrystallisation from dilute alcohol, it melted at 95° (with decomposition), and its analysis agreed with the formula $C_6H_4Me{\cdot}SO_2{\cdot}N{:}NPh$. A similar compound isomeric with the above, *p*-toluenediazobenzenesulphinate, $SO_2Ph{\cdot}N{:}N{\cdot}C_6H_4Me$, had previously been prepared by Hantzsch and Singer (*Ber.*, 1897, **30**, 312) by the action of *p*-toluenediazonium chloride on benzenesulphinic acid, and the lower homologue, $SO_2Ph{\cdot}N{:}NPh$, by Königs (*Ber.*, 1877, **10**, 1531) by the action of benzenediazonium chloride on the same substance. On the other hand, when the crude yellow product was crystallised from benzene and light petroleum, it melted sharply at 87—88°, with decomposition, and its analysis agreed with the formula $C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}N{:}NPh$.

Assuming that the diazo-sulphinate, $C_6H_4Me{\cdot}SO_2{\cdot}N{:}NPh$, had been formed in a similar way to that of Königs and of Hantzsch and Singer, we concluded that the diazoamino-compound, first formed, must have decomposed in presence of alkali into *p*-toluenesulphinic acid and phenylazoimide, and the sulphinic acid thus formed must have combined with the benzenediazonium chloride. This has been verified by carrying out the condensation in presence of a large excess of alkali, when no solid but phenylazoimide was obtained in very good yield. The sulphinic acid present in the alkaline aqueous portion was converted into the insoluble ferric salt (Thomas, T., 1909, **95**, 342). The yield was almost quantitative, according to equation (1). In another experiment the sulphinic acid was condensed with a molecular proportion of the diazonium salt, when the diazosulphinate was obtained in very good yield, the reaction taking place according to equation (2).

$$R{\cdot}SO_2{\cdot}NH_2 + R'N{:}NCl = R{\cdot}SO_2H + R'N_3 + HCl \quad . \quad . \quad (1)$$

$$R{\cdot}SO_2H + R'N{:}NCl = R{\cdot}SO_2{\cdot}N{:}NR' + HCl \quad . \quad . \quad . \quad . \quad (2)$$

Hinsberg's product may therefore be regarded as a mixture of the diazoamino-compound, $R{\cdot}SO_2{\cdot}NH{\cdot}N{:}NR'$, and the diazosulphinate, $R{\cdot}SO_2{\cdot}N{:}NR'$. This reaction has been studied with both benzene- and *p*-toluene-sulphonamides on the one hand, and aniline, *o*-, *m*-, and *p*-toluidines, and *p*-chloroaniline on the other. The products in all cases are similar and the reaction may be represented by equations (1) and (2). The reaction, therefore, can conveniently be utilised for the preparation of aromatic azoimides and sulphinic acids.

EXPERIMENTAL.

Action of Benzenediazonium Chloride on p-*Toluenesulphonamide.*

Experiment I.—Benzenediazonium chloride (made from aniline, 4·6 grams, hydrochloric acid, 15 c.c., and water, 25 c.c., diazotised with sodium nitrite, 3·5 grams in water, 15 c.c.) was slowly added to a well-cooled solution of 8·5 grams of *p*-toluenesulphonamide and 6 grams of sodium hydroxide in 175 c.c. of water. The mixture was stirred for about ten minutes and filtered, and the yellow, crystalline product washed with water and dried in a vacuum desiccator. The filtrate was slightly alkaline and smelt strongly of phenylazoimide. The crude product melted and decomposed at 83—85° (Found : N = 13·9 per cent.). The yield was 8 grams. A portion, recrystallised from aqueous alcohol, formed yellow needles, m. p. 95° with decomposition (Found : C = 59·78 by the wet method; N = 10·98; S = 12·34. *Benzenediazo*-p-*toluenesulphinate*, $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}N{:}NPh$, requires C = 60·00; N = 10·77; S = 12·31 per cent.). The sulphur was estimated by fusion with potassium carbonate and potassium nitrate, as an attempt by the Carius method resulted in an explosion just after the tube had been sealed.

The diazo-sulphinate, on reduction with zinc dust and acetic acid in alcoholic solution (Königs, *loc. cit.*), gave the colourless dihydro-derivative. This, when recrystallised from alcohol, formed needles, m. p. 154° with decomposition (Found: N = 10·9. $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}NHPh$ requires N = 10·7 per cent.).

A small portion of the crude condensation product, m. p. 83—85°, mentioned above, was dissolved in a large volume (1 gram in 50 c.c.)

of benzene at about 30° and filtered. The pale yellow, crystalline precipitate that separated on adding light petroleum to the cooled filtrate was quickly collected and dried in the dark; it melted sharply with decomposition at 87—88° (Found: N = 15·55. The diazoamine, $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}N{:}NPh$ requires N = 15·27 per cent.). When warmed with sodium hydroxide solution, contrary to Hinsberg's statement, it liberated phenylazoimide. In alcoholic solution, it gave a deep red coloration with a solution of β-naphthol.

Experiment II.—In this experiment the reaction was carried out in presence of a large excess of alkali. Benzenediazonium chloride (made from 9·3 grams of aniline) was slowly added to a solution of 17 grams of *p*-toluenesulphonamide and 15 grams of sodium hydroxide in 350 c.c. of water. In this case no precipitate was formed, but an orange, opalescent liquid was obtained smelling strongly of phenylazoimide. A drop of the liquid produced a deep red coloration on β-naphthol test-paper. A few c.c. of the liquid were acidified with cold dilute acetic acid and gave a pale yellow precipitate, which, after being filtered, washed, and dried, melted with decomposition at 85—86° (Found: N = 15·28 per cent.). The reaction mixture, which evidently contained the diazoamine in solution, showed no appreciable decomposition even after being stirred for two hours. The mixture having been kept overnight in the ice box, a considerable amount of oil had accumulated at the bottom of the vessel, but the liquid still gave the red coloration with β-naphthol test-paper. Sodium hydroxide (15 grams) was then added and the mixture stirred until no colour reaction was obtained with β-naphthol paper. It was then extracted with ether, the ether distilled off, and the residue distilled in steam. The steam distillate was again extracted with ether, and the extract dried over calcium chloride and distilled in a vacuum from a water-bath. The yield of phenylazoimide was 9 grams, the calculated yield being 11·9 grams according to equation (1). It is a clear yellow liquid, having a characteristic, penetrating, but not unpleasant smell. It explodes when heated in a test-tube over a Bunsen flame, but distils at 81° under 44 mm. pressure. To identify the product further, it was condensed with ethyl acetate, a substance, melting at 115°, being produced identical with that obtained by Dimroth (*Ber.*, 1902, **35**, 4057) from phenylazoimide and ethyl acetate.

The aqueous solution left after the phenylazoimide had been removed was divided into two equal portions. One portion was acidified with hydrochloric acid. The brick-red precipitate obtained by the addition of ferric chloride to the acid solution was collected (yield 8·5 grams, the calculated yield being 8·7 grams), treated with a slight excess of aqueous ammonia, and filtered. On the addition of concentrated hydrochloric acid to the cooled filtrate, colourless, crystalline *p*-toluenesulphinic acid was precipitated. It was recrystallised from water and melted at 86—87° (Thomas gives m. p. 86—87°, *loc. cit.*). It gave the characteristic blue colour reaction of aromatic sulphinic acids with concentrated sulphuric acid and anisole (Smiles and Rossignol, T., 1906, **89**, 696) (Found : S = 20·54. Calc., S = 20·51 per cent.).

The other portion of the aqueous solution mentioned above was treated with half the quantity of benzenediazonium chloride, when a yellow, crystalline precipitate was obtained. This was filtered off, washed with water, and dried; the yield of crude product was 13 grams (m. p. 91°), the theoretical yield being 14 grams. On recrystallisation from dilute alcohol it formed yellow needles, m. p. 95°, and proved to be identical with the benzenediazo-*p*-toluenesulphinate described in experiment I.

Action of o-*Toluenediazonium Chloride on* p-*Toluenesulphonamide.*

In this and the following experiments with *p*-toluenesulphonamide, 17 grams of the substance were dissolved in an alcoholic solution of 20 grams of potassium hydroxide, the alcohol was distilled off in a vacuum, and the residue dissolved in 150 c.c. of water. This process has the advantage that the bulk of the solution is smaller than in the previous experiments, and in spite of the large concentration of alkali the potassium salt of the sulphonamide does not separate out. *o*-Toluenediazonium chloride (made from 10·7 grams of *o*-toluidine) was then added, when a dark oil was formed. This was extracted with ether and purified as in experiment II. The yield of pure *o*-tolylazoimide was 10 grams (b. p. 90·5° at 31 mm.), the theoretical yield being 13·3 grams.

The aqueous solution was divided into two equal portions; one was treated with ferric chloride and the other with half the quantity of *o*-toluenediazonium chloride, as described in experiment II. The yield of ferric *p*-toluenesulphinate was 8 grams [Found : Fe = 10·6. $(CH_3{\cdot}C_6H_4{\cdot}SO_2)_3Fe$ requires Fe = 10·74 per cent.]. The yield of the crude *o*-toluenediazo-*p*-toluenesulphinate (m. p. 74° with decomposition) was 11 grams, the theoretical yield being 13·7 grams. On recrystallisation from alcohol, it formed deep yellow needles and melted at 95° (Found : N = 10·26.

$$CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CH_3$$

requires N = 10·22 per cent.).

Action of m-*Toluenediazonium Chloride on* p-*Toluenesulphonamide.*

The same quantities were used as in the previous experiment. The yield of pure *m*-tolylazoimide was 11 grams (b. p. 92·5° at 31 mm.), that of ferric *p*-toluenesulphinate 8·5 grams (Found: Fe = 10·65 per cent.), and that of the crude diazo-sulphinate (m. p. 62—66°) 11·5 grams. The last, on recrystallisation from alcohol, formed bright yellow needles, m. p. 72—73° (Found: N = 10·16 per cent.).

Action of p-*Toluenediazonium Chloride on* p-*Toluenesulphonamide.*

The same quantities were used. The yield of pure *p*-tolylazoimide (b. p. 93° at 32 mm.) was 10 grams. It has a characteristic aniseed smell. The yield of ferric *p*-toluenesulphinate was 8 grams (Found: Fe = 10·7 per cent.), and that of the crude diazo-sulphinate (m. p. 96—99°) was 12 grams. The latter, on recrystallisation from alcohol, formed bright yellow needles which melted at 100° with decomposition (Found: N = 10·59 per cent.).

Action of p-*Chlorobenzenediazonium Chloride on* p-*Toluenesulphonamide.*

The yellow, crystalline precipitate formed on the addition of *p*-chlorobenzenediazonium chloride (made from 12·7 grams of *p*-chloroaniline) to the solution of the sulphonamide decomposed very slowly with the separation of an oil. After remaining overnight, the mixture was extracted with ether and the extract purified as before. The yield of *p*-chlorophenylazoimide (b. p. 90—91° at 15 mm.) was 8 grams, the calculated yield being 15 grams. The aqueous portion was divided into two equal parts and treated as before. The yield of ferric *p*-toluenesulphinate was 5 grams (Found: Fe = 10·67 per cent.), that of the crude *p*-chlorobenzenediazo-*p*-toluenesulphinate, m. p. 112—117°, was 8 grams, the calculated yield being 14·7 grams. The latter, on recrystallisation from alcohol, formed golden-yellow plates, m. p. 118° with decomposition (Found: N = 9·7 per cent. $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N{:}N \cdot C_6H_4Cl$ requires N = 9·5 per cent.).

Action of Benzenediazonium Chloride on Benzenesulphonamide.

In this and the following experiments 15·7 grams of the sulphonamide were dissolved in alcoholic potassium hydroxide, and the aqueous solution was prepared as before. Molecular quantities of the various diazo-salts were used. With benzenediazonium chloride, the yield of pure phenylazoimide was 8 grams. The aqueous portion was also treated as before. The yield of ferric benzenesulphinate was 7 grams, the calculated yield being 8 grams (Found: Fe = 11·48. Calc., Fe = 11·69 per cent.). The free sulphinic acid obtained from it melted at 83—84° (Thomas gives m. p. 85°; *loc. cit.*).

The yield of the crude benzenediazobenzenesulphinate was 12 grams, the theoretical yield being 14·7 grams. On recrystallisation from dilute alcohol, it formed orange plates which melted at 75—76° with decomposition (Königs gives m. p. 75—76°; *loc. cit.*) (Found: C = 58·37; N = 11·8. Calc., C = 58·54; N = 11·38 per cent.). On reduction with zinc dust and acetic acid, it gave the dihydro-derivative, which, on recrystallisation from alcohol, formed colourless needles and melted at 158° (Königs gives m. p. 148°) (Found: N = 11·7. Calc., N = 11·3 per cent.).

Action of o-*Toluenediazonium Chloride on Benzenesulphonamide.*

The yield of pure *o*-tolylazoimide was 10 grams, that of ferric benzenesulphinate 6·5 grams (Found: Fe = 11·47 per cent.), and that of the crude *o*-toluenediazobenzenesulphinate 9·6 grams, the calculated yield being 13 grams. The last, on recrystallisation from alcohol, formed salmon-coloured, small prisms which melted with decomposition at 59—60° (Found: N = 10·6. $CH_3{\cdot}C_6H_4{\cdot}N{:}N{\cdot}SO_2Ph$ requires N = 10·77 per cent.).

Action of m-*Toluenediazonium Chloride on Benzenesulphonamide.*

The yield of pure *m*-tolylazoimide, b. p. 78° at 14 mm., was 9 grams, that of ferric benzenesulphinate 6·4 grams (Found: Fe = 11·48 per cent.), and that of the crude diazo-sulphinate 9·6 grams. The last, on recrystallisation from alcohol, formed yellow prisms which melted at 58° with decomposition (Found: N = 10·78 per cent.).

Action of p-*Toluenediazonium Chloride on Benzenesulphonamide.*

The yield of pure *p*-tolylazoimide was 9 grams, that of ferric benzenesulphinate 5·6 grams (Found: Fe = 11·48 per cent.), and that of the diazo-sulphinate 9·2 grams. The last, on recrystallisation from alcohol, formed golden-yellow prisms which melted at 85—86° with decomposition (Found: N = 10·8 per cent.); Hantzsch and Singer give m. p. 90° (*loc. cit.*).

Action of p-*Chlorobenzenediazonium Chloride on Benzenesulphonamide.*

The yellow, crystalline diazoamine formed in this experiment appeared to be rather stable. After stirring for two hours, it was filtered, washed, and dried. It melted indefinitely at about 85° (Found: N = 14·41. $SO_2Ph{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_4Cl$ requires N = 14·21 per cent.).

In another experiment, the reaction mixture was stirred for two days, when an oily liquid separated, which was extracted and purified in the usual way. The yield of pure *p*-chlorophenylazoimide was 7 grams. The aqueous portion was divided into two equal parts and treated as before. The yield of ferric benzenesulphinate was 5 grams, and that of the crude diazo-sulphinate 7 grams, the theoretical yield of the latter being 14 grams. On recrystallisation from alcohol, it formed deep yellow prisms, m. p. 106° with decomposition; Hantzsch and Singer give m. p. 102—103° (Found: N = 10·2. Calc., N = 9·98 per cent.).

In conclusion, we wish to express our thanks to Professor J. B. Cohen, F.R.S., for valuable criticism and to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

THE ORGANIC CHEMICAL LABORATORIES,
THE UNIVERSITY, LEEDS. [*Received, September 10th,* 1921.]

CCXLII.—*The Optically Active Forms of the Keto-dilactone of Benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic Acid.*

By WILLIAM HOBSON MILLS and CHARLES REYNOLDS NODDER.

IN a preliminary communication (T., 1920, **117**, 1407) we described the resolution of the keto-dilactone of benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic acid (I) into optically active components, by which an experimental demonstration was given of a previously unrealised type of molecular asymmetry associated with *spiro*cyclic constitution.*

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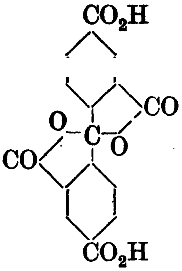
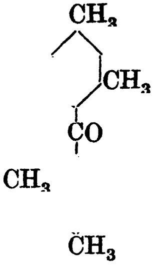
* Leuchs and Gieseler have, however, shown (*Ber.*, 1912, **45**, 2114) that bis-δ-bromo-γ-valerolactone-αα-spirane, which contains two similarly situated asymmetric carbon atoms as well as the spirane carbon atom, exists in three optically inactive forms.



(I.)



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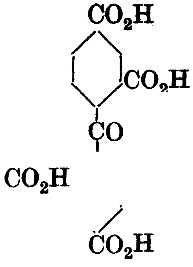
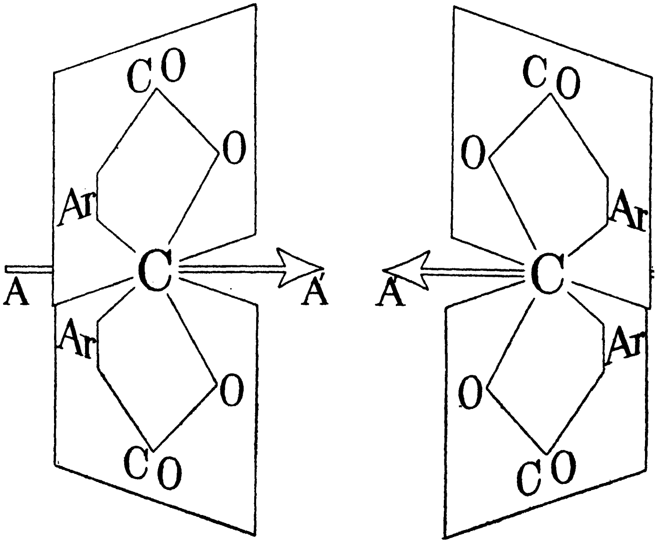


(III.)

Like methyl*cyclo*hexylideneacetic acid (Perkin, Pope, and Wallach, T., 1909, **95**, 1789), 4-oximino*cyclo*hexanecarboxylic acid (Mills and Bain, T., 1910, **97**, 1866), *d*- and *l*-inositol (Maquenne, *Ann. Chim. Phys.*, 1893, [vi], **29**, 271; Tanret, *Compt. rend.*, 1899, **109**, 908) and triethylenediaminecobaltic bromide (Werner, *Ber.*, 1912, **45**, 121) and certain analogous co-ordination compounds, this substance affords an example of an optically active compound which contains no asymmetric atom in the ordinary sense.

As regards its chemical structure, the compound is highly symmetrical; the molecule is divisible at the central spirane carbon atom into two identical halves. The molecular asymmetry is due to the fact that these two halves lie in planes which intersect—according to the theory of van't Hoff, at right angles—so that the molecule possesses as its sole element of symmetry a binary axis of the first order *AA′* and is therefore non-superposable on its mirror image (in the diagram *Ar* represents the aromatic residue $C_6H_3\cdot CO_2H$).



The relationship between the two enantiomorphous forms is somewhat similar to that between a right-handed, two-bladed screw propeller and its left-handed analogue.

Benzophenonetetracarboxylic acid (Mills, *Proc. Camb. Phil. Soc.*, 1915, **18**, 149), from which the active keto-dilactonic acids are derived, was obtained by the oxidation of di-*m*-xylyl ketone. Since the latter compound was prepared by the condensation of *m*-xylene with carbonyl chloride, there can be little doubt that it possesses the formula II, and therefore that benzophenonetetracarboxylic acid and its keto-dilactone have the constitutions III and I. An experimental proof of the correctness of these formulæ is given below.

The oxidation of the ketone was carried out in two stages. By prolonged boiling with dilute nitric acid a mixture of acids was obtained which apparently consisted chiefly of dibasic acids. These were then oxidised to the tetrabasic acid with potassium permanganate. The conversion of the easily soluble tetrabasic acid into its sparingly soluble keto-dilactone was readily effected by heating with hydrochloric acid. The keto-dilactonic acid melts at 409°.

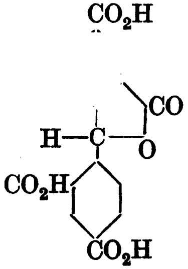
We have now carried out the resolution of the keto-dilactonic acid with considerably larger quantities of material than before, and have obtained both the dextro- and the lævo-form in what we believe to be a state of optical purity. Phenylethylamine was again employed for the resolution. The enantiomeric forms of this substance are probably the most readily accessible of the synthetic optically active bases (Lovén, *J. pr. Chem.*, 1905, [ii], **72**, 307), and may prove of service for the resolution of acids in many other cases where the natural alkaloids fail. To obtain the *d*-acid, the inactive acid was combined in the cold with the equivalent quantity of the *l*-base under such conditions that a little more than half the total quantity of salt crystallised. This was decomposed in the cold with hydrochloric acid, and the liberated acid was combined again in the same way with more *l*-base, and the process was repeated seven times. This method was employed because it involved no elevation of temperature, for the lactone rings are rather readily opened.

The *l*-acid was isolated by combining the inactive acid with *d*-phenylethylamine and recrystallising the salt repeatedly from methyl alcohol and ether until it gave an acid of constant specific rotation. In spite of the warming required this method of resolution is at least as effective as the other.

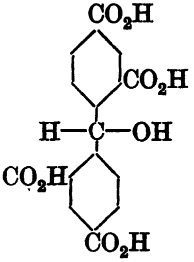
The specific rotation of the active keto-dilactonic acids in methyl ethyl ketone solution was found to be comparatively low and to vary considerably with the concentration, being greater in more concentrated solutions. For the *d*-acid was found $[\alpha]_D$ 19·5° at a concentration of 7·76 grams per 100 c.c., and for the *l*-acid at the same concentration (by interpolation) $[\alpha]_D$ − 19·53°. It has already been stated (T., 1920, **117**, 1409) that the solubility of the optically active modifications in methyl ethyl ketone is much greater than that of the inactive acid, as is strikingly shown by the abundant precipitate of the inactive acid which is immediately formed when strong solutions of the *d*- and *l*-acids are mixed. This shows that the inactive acid is a racemic substance. The *l*-acid melts at 407°. The melting point of the active form is thus 2° lower than that of the racemic acid.

Treatment of the compound with excess of alkali very rapidly opens the keto-dilactonic rings, and in consequence the rotatory power of the active modifications disappears completely when they are dissolved in sodium hydroxide solution. Even in the presence of sodium hydrogen carbonate the rotatory power gradually falls to zero. The specific rotation of the sodium salt in aqueous solution is in the opposite sense to that of the free keto-dilactonic acid in methyl ethyl ketone and has a much smaller value.

We have also resolved the lactone of benzhydrol-2 : 4 : 2′ : 4′-tetracarboxylic acid (IV) and have investigated its oxidation to



(IV.)

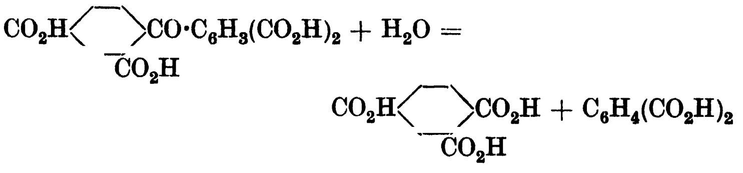


(V.)

find whether the optically active keto-dilactonic acid could be produced in this manner. The inactive lactonic acid was obtained by dissolving the keto-dilactonic acid in excess of ammonia and reducing with zinc dust. The benzhydroltetracarboxylic acid thus produced is transformed into its lactone with the greatest readiness when set free from its salts. The lactonic acid was resolved by means of brucine. From an alcoholic solution of equivalent quantities of the acid and brucine the brucine salt of the *l*-acid crystallised out very slowly, and on decomposition gave an acid showing the specific rotation $[\alpha]_D$ − 258° in methyl ethyl ketone solution. The specific rotation of this compound, which contains an ordinary asymmetric carbon atom, is thus very much higher than that of the chemically closely related but centro-asymmetric keto-dilactonic acid.

It was found that the oxidation to the keto-dilactonic acid could be effected by chromic acid in glacial acetic acid solution. However, the product obtained from the optically active lactonic acid proved to be inactive. This is not surprising, for since the reaction involves the oxidation of a hydrogen atom attached to the asymmetric carbon atom, the change would be expected to be associated with much racemisation.

The optically active lactonic acid loses its activity completely when dissolved in excess of sodium hydroxide solution, showing that when the lactone ring is opened the central carbon atom ceases to be asymmetric. This fact is important, because it allows the conclusion to be drawn that in benzhydroltetracarboxylic acid (V), and consequently also in benzophenonetetracarboxylic acid, the two residues, $\cdot C_6H_3(CO_2H)_2$, are alike; and when this is established the constitution of the two acids becomes comparatively easy to determine. For when benzophenonetetracarboxylic acid is fused with sodium hydroxide, it undergoes hydrolysis, giving a mixture of two acids. The less soluble of these was readily identified as *iso*phthalic acid. The more soluble had the composition of a benzenetricarboxylic acid, $C_6H_3(CO_2H)_3$, and when heated gave an anhydride, $C_6H_3(C_2O_3)\cdot CO_2H$. It was therefore either hemimellitic or trimellitic acid. The melting point of the acid was 228—230° and of the anhydride 159—162°. These are the melting points of trimellitic acid and of its anhydride.* The more soluble acid was accordingly trimellitic acid. Hence the hydrolysis must proceed in accordance with the equation:



$$CO_2H\underset{CO_2H}{\langle\quad\rangle}CO\cdot C_6H_3(CO_2H)_2 + H_2O =$$

$$CO_2H\underset{CO_2H}{\langle\quad\rangle}CO_2H + C_6H_4(CO_2H)_2$$

for, since benzophenonetetracarboxylic acid was prepared from *m*-xylene, the two carboxyl groups attached to each nucleus in the molecule of this acid must be in the *meta*-position to one another.

The constitution of one half of the molecule is thus fixed and, since the two halves have been shown to be alike, the constitution II assigned to the acid is therefore established.

EXPERIMENTAL.

Di-m-*xylyl Ketone*.—The preparation of a dixylyl ketone by leading carbonyl chloride into cooled "xylol" and treating the solution with aluminium chloride was briefly described by Ador and Rilliet (*Ber.*, 1878, **11**, 399); we have, however, been able to find no record in the literature of the preparation of pure di-*m*-xylyl ketone. It can be readily obtained in the following manner. Liquid carbonyl chloride (14·25 c.c.) is allowed to evaporate slowly into a mixture of *m*-xylene (50 grams), carbon disulphide (120 c.c.), and aluminium chloride (63 grams) cooled in ice. The greater part of the aluminium chloride dissolves and the liquid separates into two layers, the lower of which is dark coloured and contains the aluminium chloride compound of the ketone. After forty-eight hours, the mixture is poured on to ice. The aqueous layer is separated, the lower layer, which consists of a carbon disulphide solution of the product, is added to dilute hydrochloric acid, and a current of steam is led in to remove the carbon disulphide and unchanged *m*-xylene and decompose traces of xyloyl chloride. The crude ketone which remains is dissolved in ether and after washing with alkali, drying, and removal of the ether, is distilled under diminished pressure. At 17 mm. nearly the whole distils at 200—201° (Found: $C = 85{\cdot}6$; $H = 7{\cdot}7$. $C_{17}H_{18}O$ requires $C = 8{\cdot}7$; $H = 7{\cdot}5$ per cent.). The yield of pure ketone is about 70 per cent. of the *m*-xylene taken.

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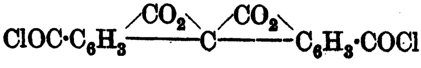
* Hemimellitic acid melts at 190° and its anhydride at 196°.

Keto-dilactone of Benzophenone-2 : 4 : 2′ : 4′-*tetracarboxylic Acid.*— The ketone (10 grams) was boiled with dilute nitric acid (120 c.c.) obtained by mixing the concentrated acid (*d* 1·42) with 6 volumes of water. The boiling was continued until the greater part of the oil had become soluble in aqueous sodium carbonate solution. The rate of oxidation varied considerably in different experiments, but usually two to three days' boiling was required. The product was a faintly yellow oil which solidified on cooling. It was dissolved in ether and the acids which had been formed were extracted from the ethereal solution with aqueous sodium carbonate solution. These contained a certain amount of nitro-acids which it was essential to remove. This was done by reduction with ferrous hydroxide. A solution of the acids in an excess of sodium hydroxide was added to a solution of ferrous sulphate, containing 10 grams of the crystallised salt for the acids from each 10 grams of ketone, and the mixture was digested for five hours on the water-bath. After cooling, it was acidified with hydrochloric acid and the precipitated acids were taken up in ether. On titration of the acids thus obtained, the volume of normal alkali required to neutralise 1 gram was found to range from 6·22 c.c. to 7·22 c.c., the average being 6·8 c.c. For 1 gram of an acid formed by the conversion of two of the methyl groups of dixylyl ketone into carboxyl groups the volume of normal alkali required would be 6·71 c.c. It would appear, therefore, that the oxidation with dilute nitric acid leads to the formation chiefly of such dibasic acids.

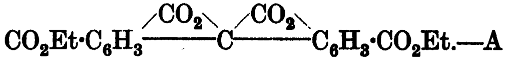
As the product was presumably a mixture, it was not further investigated, but was at once oxidised to the tetrabasic acid with potassium permanganate. From the alkali equivalent the quantity of permanganate required for the oxidation was calculated, and an amount 10 per cent. in excess of this was added in 5 per cent. solution to the boiling solution of the acids in potassium hydroxide. The permanganate was added in small quantities until decolorisation became slow. The remainder was then added all at once and the mixture gently boiled for six hours. The tetrabasic acid is a comparatively soluble compound which is precipitated by hydrochloric acid as a viscid oil from not too weak solutions of its salts. Addition of excess of hydrochloric acid salts out more of the acid, but the precipitate dissolves again on warming. If this solution is now heated to boiling, the keto-dilactonic acid separates gradually as a colourless, dense, crystalline powder. The filtrate from the manganese dioxide was therefore concentrated, strongly acidified with hydrochloric acid, and heated on the water-bath until the separation of the keto-dilactonic acid was complete. The yield is fairly satisfactory. For example, in one series of experiments, 30 grams of the keto-dilactonic acid were obtained from 34 grams of dixylyl ketone.

The compound is exceedingly sparingly soluble in most of the common solvents, acetone and methyl ethyl ketone being those by which it is most readily dissolved. Small quantities can be recrystallised from boiling glacial acetic acid. The melting point observed with a mercury thermometer immersed to the zero mark in a bath of mixed sodium and potassium nitrates was 390°. The corrected value is 409° (Found: $C = 59{\cdot}8$; $H = 2{\cdot}5$. $C_{17}H_8O_8$ requires $C = 60{\cdot}0$; $H = 2{\cdot}4$ per cent.). The compound dissolves in cold sodium hydrogen carbonate solution without the lactone rings being opened to any great extent, and is immediately reprecipitated when the solution is acidified. If the solution in sodium hydrogen carbonate, however, has been boiled, or if the substance has been dissolved in sodium hydroxide solution, the lactone rings are opened and on acidification no precipitate, or in stronger solutions an amorphous precipitate of the tetrabasic acid, is obtained.

The following derivatives of the keto-dilactonic acid illustrate the stability of the keto-dilactonic group. For assistance with the preparation and investigation of these our thanks are due to Mr. A. F. R. Evans.



The Acid Chloride, $\mathrm{ClOC{\cdot}C_6H_3\overset{\diagup CO_2 \diagdown}{\text{———}}C\overset{\diagup CO_2 \diagdown}{\text{———}}C_6H_3{\cdot}COCl}$.—The keto-dilactonic acid (15 grams) was moistened with phosphoryl chloride and heated for three hours at 100—120° with phosphorus pentachloride (19·2 grams). The phosphoryl chloride was removed by distillation under diminished pressure, and the residue crystallised from toluene. The compound consists of colourless needles melting at 187° (Found: Cl = 18·86. $C_{17}H_6O_6Cl_2$ requires Cl = 18·83 per cent.).

The Ethyl Ester,  $CO_2Et{\cdot}C_6H_3\overset{\diagup CO_2 \diagdown}{\overline{\qquad\quad}}C\overset{\diagup CO_2 \diagdown}{\overline{\qquad\quad}}C_6H_3{\cdot}CO_2Et$.—A solution of the acid chloride in benzene was heated with excess of absolute alcohol. The ester was deposited on cooling, and after recrystallisation from alcohol and benzene melted at 215—217°. It is rather sparingly soluble in hot alcohol or acetone; it dissolves much more readily in benzene (Found: C = 63·7; H = 4·0. $C_{21}H_{16}O_8$ requires C = 63·6; H = 4·0 per cent.).

Resolution of the Keto-dilactonic Acid.

The d-*Keto-dilactonic Acid.*—The keto-dilactonic acid (8·43 grams) was suspended in methyl alcohol (100 c.c.) and a solution of *l*-α-phenylethylamine (6·0 grams), of specific rotation $[\alpha]_D^{12\cdot5^\circ} - 40\cdot4^\circ$, in methyl alcohol (5 c.c.) was added drop by drop. When all the base had been introduced, dry ether (105 c.c.)was added. After stirring for ten minutes, the crystalline salt was collected. It weighed 8·5 grams. The keto-dilactonic acid was then liberated by digesting with dilute hydrochloric acid (*d* 1·08). After careful washing with water, it was dried, and weighed 4·9 grams. This acid was again combined with the *l*-base as before and the whole process was repeated a number of times. After the fourth salt-formation the keto-dilactonic acid gave the following data when polarimetrically examined in methyl ethyl ketone solution; 1·617 grams in 13·1 c.c. gave $\alpha_D^{16^\circ} + 4\cdot55^\circ$ ($l = 2$), whence $[\alpha]_D^{16^\circ} + 18\cdot4^\circ$. After a fifth salt-formation, 1·0153 grams in 13·1 c.c. gave $\alpha_D^{15^\circ} + 2\cdot95^\circ$ ($l = 2$), whence $[\alpha]_D^{15^\circ} + 19\cdot03^\circ$. After the acid had been subjected to a seventh salt-formation, the salt was recrystallised from hot methyl alcohol with subsequent addition of ether. The liberated acid (0·5181 gram) in 6·68 c.c. of methyl ethyl ketone gave $\alpha_D^{15^\circ} + 1\cdot51^\circ$ ($l = 1$), whence $[\alpha]_D^{15^\circ} + 19\cdot5^\circ$. This value agrees with that of the optically pure *l*-acid.

The l-*Keto-dilactonic Acid.*—The keto-dilactonic acid (18·4 grams) was suspended in methyl alcohol (180 c.c.) and a solution of *d*-α-phenylethylamine (13·1 grams), of specific rotation $[\alpha]_D^{12\cdot5^\circ} + 40\cdot4^\circ$, in methyl alcohol (20 c.c.) was added drop by drop. After all the base had been introduced, anhydrous ether (160 c.c.) was added.

Stirring was continued for fifteen minutes. The salt thus obtained (16·6 grams) was recrystallised from methyl alcohol (350 c.c.) and ether (550 c.c.). The weight of the recrystallised salt was 7·0 grams. After two further recrystallisations from methyl alcohol and ether, 4·8 grams of salt were obtained. Of this 1·8 grams were decomposed with dilute hydrochloric acid and the resulting acid was examined in the polarimeter; 1·05 grams in 13·1 c.c. of methyl ethyl ketone gave $\alpha_D^{13°} - 3·15°$ ($l = 2$), whence $[\alpha]_D^{13°} - 19·65°$. The remainder of the salt (3 grams) was again crystallised from methyl alcohol (80 c.c.) and ether (200 c.c.). Of the resulting 2·4 grams, 1·9 grams were decomposed. The acid obtained (1·05 grams) in 13·1 c.c. of methyl ethyl ketone gave $\alpha_D^{15°} - 3·15°$ ($l = 2$), whence $[\alpha]_D^{15°} - 19·65°$. A fourth recrystallisation of the salt had failed therefore to produce any further rise in optical rotatory power, and it was concluded that the optically pure *l*-acid had been obtained.

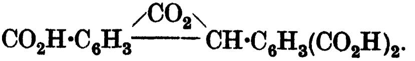
The specific rotation in methyl ethyl ketone solution varies considerably with the concentration. This is shown by the following observations on the pure *l*-acid.

1·48 grams in 13·1 c.c. gave $\alpha_D^{15°} - 4·62°$ ($l = 2$),
whence $[\alpha]_D^{15°} - 20·44°$.
0·45 gram in 13·1 c.c. gave $\alpha_D^{15°} - 1·22°$ ($l = 2$),
whence $[\alpha]_D^{15°} - 17·76°$.

The *l*-acid melts at 407° (corrected).

Action of Sodium Hydrogen Carbonate.—The effect of a solution of sodium hydrogen carbonate on the active acid was examined in order to investigate the stability of the keto-dilactonic rings towards this reagent. The pure lævo-acid (0·452 gram) was dissolved in a solution of sodium hydrogen carbonate (0·82 gram, that is, rather more than three and a half times the equivalent quantity) and the solution was diluted to a volume of 13·1 c.c. and examined in the polarimeter as rapidly as possible. The observed rotation was $\alpha_D^{15°} + 0·18°$ ($l = 2$). Thus the *l*-acid gave a dextrorotatory sodium salt. After one hour, the same solution showed $\alpha_D^{16°} + 0·10°$ ($l = 2$). After eighteen hours, the activity had disappeared.

Lactone of Benzhydrol-2 : 4 : 2′ : 4′-tetracarboxylic Acid.



$$CO_2H\cdot C_6H_3\overset{CO_2}{\overline{\qquad\qquad}}CH\cdot C_6H_3(CO_2H)_2.$$

This compound was prepared by reducing the keto-dilactonic acid with zinc dust and ammonia. The keto-dilactonic acid (4 grams) was dissolved in aqueous ammonia, *d* 0·88 (40 c.c.), and zinc dust (12 grams) was added in three portions at intervals of twenty minutes while the mixture was heated on the water-bath. The precipitate obtained by acidifying the filtrate from the excess of zinc dust was crystallised from 60 per cent. acetic acid. The keto-dilactonic acid can also be readily reduced to the lactonic acid by suspending it in 50 per cent. acetic acid and heating with excess of zinc dust. The lactonic acid crystallises in slender needles melting at 309—311° (Found: $C = 59{\cdot}4$; $H = 3{\cdot}1$. $C_{17}H_{10}O_8$ requires $C = 59{\cdot}6$; $H = 2{\cdot}9$ per cent.). When a solution of the lactonic acid in aqueous sodium hydroxide solution is acidified with dilute sulphuric acid, no precipitate appears at first; after a short time, however, a gradual deposition of the lactonic acid begins, the separation being greatly accelerated by heating the solution.

Resolution of the Lactonic Acid.—The acid (5·13 grams) and anhydrous brucine (7 grams) were dissolved in rectified spirit (1200 c.c.) and the solution was inoculated with crystals of the salt which had been obtained previously. The liquid was allowed to evaporate slowly for six weeks; its volume had then become reduced to about one half and a crop of crystals of brucine salt had been deposited. By decomposition of this salt with dilute hydrochloric acid (*d* 1·08) and careful removal of the brucine, 2·65 grams of lactonic acid were obtained, which proved to be strongly lævorotatory.

0·3046 Gram in 13·1 c.c. of methyl ethyl ketone gave $\alpha_D^{16^\circ} - 11{\cdot}97^\circ$ ($l = 2$), whence $[\alpha]_D^{16^\circ} - 258^\circ$.

0·2 Gram in 30 c.c. of acetone gave $\alpha_D^{15^\circ} - 6{\cdot}13^\circ$ ($l = 4$), whence $[\alpha]_D^{15^\circ} - 229{\cdot}9^\circ$.

This *l*-acid (0·3 gram) was dissolved in dilute aqueous sodium hydroxide solution (13·1 c.c.) and examined in the polarimeter. No trace of optical activity could be observed. The *l*-lactonic acid is much more soluble in alcohol than the inactive form. It crystallises from 50 per cent. alcohol in hemispherical aggregates of small needles. The acid recovered from the mother-liquor from which the brucine salt had crystallised showed a small dextrorotation.

Fusion of the Keto-dilactonic Acid with Potassium Hydroxide.

The keto-dilactonic acid (3 grams) was dissolved in a little aqueous potassium hydroxide solution, and added to solid potassium hydroxide (40 grams), and the mixture was heated at 280—285° for three hours. When cold, the melt was dissolved in water, dilute sulphuric acid was added so as to leave the liquid slightly alkaline, and the precipitated potassium sulphate was removed. The filtrate was then acidified, when a sparingly soluble acid was precipitated, the weight of which, after recrystallisation from dilute alcohol, was 1·1 grams. This was shown to be *iso*phthalic acid. After purification by distillation and further recrystallisation, it melted at 324° (uncorr.), and a specimen of pure *iso*phthalic acid prepared by the oxidation of *m*-xylene, as well as a mixture of the two preparations, melted at the same temperature. The equivalent was found to be 83·8 (calc., 83). The methyl ester, prepared by heating the acid with methyl alcohol and sulphuric acid, melted at 62·5° (the ester apparently contained a trace of a less soluble impurity and the melting point was not raised by repeated crystallisation). The melting point of a mixture of this ester with pure methyl *iso*phthalate, which melts at 63—64°, was 62·5°.

Trimellitic Acid.—The filtrate from the crude *iso*phthalic acid was saturated with ammonium sulphate and extracted three times with ether. By evaporation of the ether an acid was obtained which was readily soluble in water. To separate from traces of *iso*phthalic acid this was converted into its barium salt (barium *iso*phthalate is easily soluble in water) by heating its solution in dilute ammonia with barium chloride. The barium salt was slowly deposited from the hot solution. It was collected, redissolved in dilute hydrochloric acid, and reprecipitated by heating after neutralising with ammonia. The acid was isolated from the barium salt by dissolving in hydrochloric acid and extracting with ether. The acid thus obtained weighed 0·85 gram, the purification through the barium salt being attended with considerable loss. It was recrystallised by dissolving in hot water (3 c.c.) and adding concentrated hydrochloric acid (4·5 c.c.) (Found: C = 51·24; H = 3·1. Calc., C = 51·4; H = 2·9 per cent.).

The acid melted at 228—230°. Ekstrand gives 228° as the melting point of trimellitic acid (*J. pr. Chem.*, 1891, [ii], **43**, 429), Baeyer (*Ber.*, 1899, **32**, 2445) gives 224—225°.

Trimellitic Anhydride.—The acid was heated in a bath at 210—220° under diminished pressure (2 mm.), when the anhydride sublimed (Found: C = 56·0; H = 2·2. Calc., C = 56·25; H = 2·0 per cent.). It melted at 159—162°. Baeyer (*Annalen*, 1873, **166**, 341) gives 157—158° as the melting point of trimellitic anhydride, and Schultze (*Annalen*, 1908, **359**, 142) gives 162·5—163·5°.

One of us (C. R. N.) is indebted to the Department of Scientific and Industrial Research for a grant, for which he desires to express his thanks.

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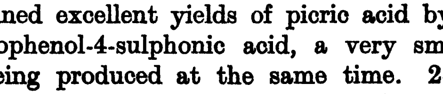
CCXLIII.—*Production of Picric Acid from the Sulphonic Acids of Phenol.*

By Ruth King.

The preparation of picric acid from phenol by the successive action of sulphuric and nitric acids has engaged a considerable amount of attention. Since better yields of picric acid are usually produced when an amount of sulphuric acid is employed sufficient to give a very considerable proportion of phenol-2 : 4-disulphonic acid, the view that the formation of this acid is necessary before proceeding to nitration has been accepted in many quarters as correct.

That the certainty of a good yield is increased by the disulphonation of phenol has been confirmed by Marqueyrol, Carré, and Loriette (*Bull. Soc. chim.*, 1920, [iv], **27**, 143), but the fact remains that in some manufacturing processes good yields are obtained from mixtures containing a considerable amount of phenol-4-sulphonic acid, so that evidently high sulphonation is not the only factor which comes into play. Phenol-4-sulphonic acid can give yields up to 79 per cent. of the theoretical, if nitrated in presence of a large excess of concentrated sulphuric acid, whilst 2-nitrophenol-4-sulphonic acid will give a yield up to 83 per cent. of that theoretically obtainable if nitrated in presence of sufficient sulphuric acid.

In the case of phenol-2 : 4-disulphonic acid, nitrolysis of the *p*-sulpho-group is preferred; if 6-nitrophenol-2 : 4-disulphonic acid is subjected to nitrolysis, the sulpho-group in position 4 is preferentially replaced and 4 : 6-dinitrophenol-2-sulphonic acid first formed.



This result is complementary to that of Marqueyrol, Carré, and Loriette (*loc. cit.*), who found that picric acid is produced more rapidly from 2 : 6-dinitrophenol-4-sulphonic acid than from the isomeric 2 : 4-dinitrophenol-6-sulphonic acid. The present author has also obtained excellent yields of picric acid by the nitrolysis of 2 : 6-dinitrophenol-4-sulphonic acid, a very small amount of oxalic acid being produced at the same time. 2-Nitrophenol-4-sulphonic acid gives more oxalic acid under the same conditions; even greater amounts are formed from phenol-4-sulphonic acid, but the quantity obtained is dependent largely on the concentration of the sulphuric acid; the greater this is, the smaller is the quantity of oxalic acid produced.

To obviate formation of oxalic acid and dinitrophenol, the latter of which shows great resistance to further nitration by diluted acids, it is essential to monosulphonate the phenol in position 4, and desirable to introduce a second sulpho-group in position 2, or, alternatively, to nitrate the phenol-4-sulphonic acid in presence of a considerable excess of sulphuric acid. Phenol-2 : 4 : 6-trisulphonic acid is prepared only by very drastic sulphonation; the amount in an ordinary sulphonation mixture is consequently negligible.

In studying the manufacture of picric acid from phenol by the usual process of successive sulphonation, dilution, and nitration, the following facts must be considered.

1. The sulphonation mixture consists almost entirely of phenol-4-sulphonic acid, phenol-2 : 4-disulphonic acid, and an excess of concentrated sulphuric acid.
2. When nitric acid acts on a phenolsulphonic acid in presence of excess of concentrated sulphuric acid, hydrogen of the nucleus is replaced by the nitro-group.
3. In presence of dilute sulphuric acid, sulpho-groups are replaced by the nitro-group.
4. In dilute acid solution, nitric acid exerts an oxidising action resulting in the formation of oxalic acid; this is the more marked as the phenol nucleus is less protected by substituents.

The author bases the views expressed above on a study of the action of diluted nitric acid in presence of sulphuric acid on the following compounds.

(*a*) Phenol-4-sulphonic acid.
(*b*) Phenol-2 : 4-disulphonic acid.
(*c*) 2-Nitrophenol-4-sulphonic acid.
(*d*) 4-Nitrophenol-2-sulphonic acid.
(*e*) 2 : 6-Dinitrophenol-4-sulphonic acid.
(*f*) 4 : 6-Dinitrophenol-2-sulphonic acid.
(*g*) 6-Nitrophenol-2 : 4-disulphonic acid.

Since the formation of phenol-2-sulphonic acid, phenol-2 : 6-disulphonic acid and phenol-2 : 4 : 6-trisulphonic acid in the sulphonation mixture is negligible, neither their nitration nor that of 4-nitrophenol-2 : 6-disulphonic acid has been studied.

EXPERIMENTAL.

(*a*) *Phenol-4-sulphonic Acid.*

This acid (Kekulé, *Zeitsch. Chem.*, 1867, 199; *Ber.*, 1869, **2**, 330; Post, *Annalen*, 1880, **205**, 64) was used in the form of its pure crystallised sodium salt; the formula assigned to it by Shadwell (*Jahresb.*, 1881, 874) was controlled (Found : $H_2O = 15·8$; $Na = 11·4$. $C_6H_5O_4SNa,2H_2O$ requires $H_2O = 15·5$; $Na = 11·7$ per cent.).

Weighed amounts of the salt, sulphuric acid, and water were treated with a known amount of nitric acid, the latter being added slowly, as the reaction is apt to be violent when much sulphuric acid is present.

All the solutions turned red. They were cooled and kept overnight. By next morning all had retained their red colour, whilst a reddish-brown solid floated on the surface, with the exception of mixtures 1 and 2 (see below), in which a yellow solid had also been deposited.

The mixtures were then heated for eight hours at 100°; oil separated in mixtures 4, 5, 6, and 7, this separation being more marked and disappearing more slowly the lower the concentration of the sulphuric acid. It was noticed that, after cooling, mixtures 1 and 2 retained a red tint, whilst mixtures 4, 5, 6, and 7 were pale yellow, this tint decreasing regularly as the ratio of water to sulphuric acid increased.

The picric acid was filtered off, washed with 60 c.c. of water, dried to constant weight at 75°, and weighed, and the melting point was determined.

No further yield of picric acid was obtained by after-nitration of the filtrate with 7 c.c. of nitric acid of 67 per cent.

Expt.	Sodium salt (0·1 mol.). Grams.	Sulphuric acid (95 per cent.). Grams.	Water. Grams.	Nitric acid (67 per cent.; 0·4 mol.). Grams.	Yield. Grams.	Yield per cent.	M. p.
1	23·2	59·6	0	39·9	18·1	79	120–121°
2	,,	60·9	10	39·1	17·4	76	120
3	,,	61·1	20	40·3	17·6	77	120
4	,,	50·8	30	39·1	17·7	77·3	120
5	,,	38·6	40	40·5	17·7	77·3	118–120
6	,,	30	50	40	16·7	73	100–113
7	,,	20	60	40	16·1	70·3	below 92

Separate experiments showed that more oxalic acid was produced in presence of dilute than of concentrated sulphuric acid.

(*b*) *Phenol*-2 : 4-*disulphonic Acid.*

The free acid is deliquescent (Griess, *Annalen,* 1866, **137**, 69; Kekulé, *Zeitsch. Chem.*, 1866, 693), but well-crystallised barium (Zingel, *Jahresb.*, 1885, 1597) and sodium salts exist. Zingel describes the barium salt as crystallising with 4 molecules of water.

The metal content was checked in an anhydrous specimen (Found: Ba = 34·2. Calc., Ba = 35·2 per cent.).

The Sodium Salt.—Direct preparation of this salt from a sulphonation mixture is usually an uncertain operation, but the following method gave good results: one hundred grams of phenol and 400 grams of oleum (23 per cent.) were heated at 100° for three and a half hours and poured into a solution of 450 grams of sodium sulphate ($Na_2SO_4,10H_2O$) in 500 c.c. of water at 32°. On the next day, the crystalline precipitate was collected, washed with a little water, and dried in the air.

The product had a slightly brown tinge and weighed 200 grams; the weight of the anhydrous product, dried at 120°, was 180 grams (about 57 per cent. of the theoretical) (Found: Na = 14·97. Calc., Na = 15·43 per cent.).

In several preparations, a colloidal mass was obtained in place of the well-defined crystals referred to above. The salt, when collected and dried, always gave results too low in sodium (Found: in different preparations, Na = 14·9, 13·6, 14·6 per cent.).

Such results would be obtained if the phenoldisulphonic acid had condensed with itself to give a diphenolsulphonetrisulphonic acid, but sulphur estimations to confirm this supposition have not been carried out.

That phenol-2:4-disulphonic acid gives good yields of picric acid remarkably free from dinitrophenol, has been established by other workers (private communication from Dr. Clarence Smith; Marqueyrol, Carré, and Loriette, *loc. cit.*).

(c) 2-*Nitrophenol*-4-*sulphonic Acid.*

This acid has been previously described as crystallising with $3H_2O$. Hydrated, it is said to melt at 51·5°; in the anhydrous condition, at 122°. It has been prepared by sulphonation of *o*-nitrophenol with fuming sulphuric acid (Kekulé, *Zeitsch. Chem.*, 1867, 64) and with chlorosulphonic acid (Armstrong, *ibid.*, 1871, 321; Mazurowska, *J. pr. Chem.*, 1876, [ii], **13**, 171), or by nitrating phenol-4-sulphonic acid (Kolbe and Graube, *Annalen*, 1868, **147**, 71; Kekulé, *Ber.*, 1869, **2**, 332; Korner, *Jahresb.*, 1872, 605). It is also obtained by the action of potassium hydroxide on 1-bromo-2-nitrobenzene-4-sulphonic acid (Goslich, *Annalen*, 1876, **180**, 105) and on 2-nitroaniline-4-sulphonic acid (Nietzki and Lerch, *Ber.*, 1888, **21**, 3221).

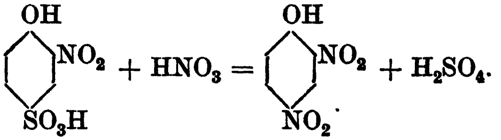
The Sodium Salt.—This was very readily prepared by the following method: 120 grams of crystallised sodium phenol-4-sulphonate dissolved in 300 c.c. of hot water were treated with 72 c.c. of nitric acid (*d* 1·4) in the course of fifteen to twenty minutes, the temperature during nitration being kept at about 60°. The reaction proceeded quite smoothly and was accompanied by slight fuming, especially towards the end of the reaction. On cooling, an orange, crystalline salt separated. In one experiment, supersaturation was very noticeable. The salt was collected and washed with a little water; the crystals became paler in colour on drying. One hundred and twenty grams of the *p*-sulphonate gave 128 grams of sodium 2-nitrophenol-4-sulphonate (about 83 per cent. of the theoretical yield). After recrystallisation, the following figures were obtained on analysis (Found: $H_2O = 18·7$; $Na = 9·50$. $C_6H_4O_6NSNa,3H_2O$ requires $H_2O = 18·7$; $Na = 9·55$ per cent.).

In the preparation described, nearly two molecular proportions of nitric acid were employed for one of sodium phenolsulphonate. With a lower proportion of nitric acid (140 c.c.) to the phenolsulphonate (300 grams), the yield was seriously reduced (150 grams).

A further quantity was recovered by evaporation, but in an impure condition. On the other hand, attempts to increase the yield by the addition of more nitric acid after the first separation of salt led to the formation of 2 : 4-dinitrophenol, so that it is obviously advisable to cool well and to recover as much of the nitrosulphonate as possible in the first instance.

In an actual experiment in which 172·8 grams of the nitrosulphonate were obtained from 250 grams of sodium phenolsulphonate, an attempt was made to recover more of the nitrosulphonate by adding a further 10 c.c. of nitric acid (*d* 1·4) to the filtrate and warming until fumes ceased to be evolved. A yellow solid separated on cooling, which was very slightly soluble in cold water and after recrystallisation from boiling water melted at 112—113°. The melting point of the mixture with an authentic specimen of 2 : 4-dinitrophenol proved the identity of the compound, of which 20 grams were obtained.

It is evident that the sodium 2-nitrophenol-4-sulphonate in the solution underwent nitrolysis by the treatment, according to the equation:



As will be seen later, 2 : 6-dinitrophenol-4-sulphonic acid may be obtained as the chief product of the reaction between 2-nitrophenol-4-sulphonic acid and dilute nitric acid, provided that an excess of sulphuric acid is present.

The Barium Salt.—This was prepared by precipitating the solution of the sodium salt with barium chloride; Kekulé's formula, $(C_6H_4O_6NS)_2Ba,H_2O$, was confirmed.

The Free Acid.—This is described in the literature as crystallising with three molecules of water. A convenient method of preparation is to dissolve the barium salt (which can readily be obtained in a state of purity) in hot water, precipitate with the calculated amount of dilute sulphuric acid, remove the barium sulphate, and evaporate the filtrate. The residue is dissolved in a small quantity of water, filtered from any residual barium sulphate, and again concentrated. Care has to be taken in concentrating, as the acid is very soluble in water, and in the hydrated condition melts at 49° (given as 51·5° in the literature). The hydrated acid forms long, pale yellow needles and dissolves in water with very marked absorption of heat. Titration (with phenolphthalein as the indicator) gave a molecular weight of 268; $NO_2\cdot C_6H_3(OH)\cdot SO_3H,H_2O$ requires $M = 272$. The end-point was difficult to determine on account of the colour of the sodium salt of the acid.

Whilst phenol-4-sulphonic acid gives poor yields of picric acid of inferior quality when nitrated in presence of much water and little sulphuric acid, 2-nitrophenol-4-sulphonic acid gives much better results under the same conditions. In the following table, the results are given of the nitration of sodium 2-nitrophenol-4-sulphonate ($+ 3H_2O$), the amounts of water and sulphuric acid being varied. The procedure adopted was that described for sodium phenol-4-sulphonate.

Nitration of 2-Nitrophenol-4-sulphonic Acid.

(Heating at 100° for eight hours.)

Expt.	Sodium salt (0·1 mol.). Grams.	Sulphuric acid (94 per cent.). Grams.	Water. Grams.	Nitric acid (67 per cent.; 0·32 mol.). Grams.	Yield. Grams.	Yield per cent.	M. p.
1	29·5	61·2	0	30	18·5	80·8	121°
2	,,	59·1	10	33·9	—	—	—
3	,,	60·5	20	30·4	17·85	78	120
4	,,	50·7	30	30·6	18·2	79·5	119–120
5	,,	44·8	40	29·5	19·1	83·5	120–121
6	,,	30	50	30	18·95	82·6	119–120
7	,,	20	60	30	18·05	78·8	118–119·5

Comparison of experiments 6 and 7 of the two series shows very plainly the great improvement effected during nitrating in presence of small amounts of sulphuric acid when the molecule of the phenolsulphonate has been stabilised by the introduction of the nitro-group. In this connexion, a pair of comparative experiments may be described.

Ninety-four grams of phenol were sulphonated with 4 mols. of sulphuric acid (408·1 grams of 96·18 per cent.) to 187·3 per cent. sulphonation. Nitric acid (1·25 mols.; 114·6 grams of 69 per cent.) was added in the cold. After mononitration, 450 c.c. of water were added, then 2·75 mols. of nitric acid, and the mixture was heated at 100° for twelve hours. The yield of picric acid (m. p. 120°) was 80·8 per cent. of the theoretical.

In the other experiment, 94 grams of phenol were sulphonated with 2 mols. of sulphuric acid to 133·2 per cent. sulphonation. After cooling, a further 2 mols. of sulphuric acid were added and then 1·75 mols. of nitric acid. After dilution with 450 c.c. of water, nitrolysis was carried out exactly as described in the previous experiment. The yield of picric acid was 79 per cent. of that theoretically possible; the acid also melted at 120°, but its appearance was inferior.

(*d*) 4-*Nitrophenol*-2-*sulphonic Acid.*

This acid has been obtained by sulphonation of *p*-nitrophenol with fuming sulphuric acid (Post, *Annalen*, 1880, **205**, 38; Korner, *Jahresb.*, 1872, 604), but not with chlorosulphonic acid (Armstrong, *Zeitsch. Chem.*, 1871, 322). Stuckenberg (*Annalen*, 1880, **205**, 45) obtained the same acid by nitration of phenol-*o*-sulphonic acid.

The first of these operations was difficult to carry out (compare Graham and Knecht, *J. pr. Chem.*, 1906, [ii], **73**, 519), the second is to be avoided on account of the difficulty in obtaining the necessary phenol-*o*-sulphonic acid. The following method has been worked out and found satisfactory.

p-Chloronitrobenzene is sulphonated (Claus and Mann, *Annalen*, 1891, **265**, 88; P. Fischer, *Ber.*, 1891, **24**, 3194) and 1-chloro-4-nitrobenzene-2-sulphonic acid isolated. It is unnecessary to follow Claus and Mann in first preparing the barium salt if the following method is adopted:—100 grams of *p*-chloronitrobenzene and 600 grams of fuming sulphuric acid (10—12 per cent. of SO_3) were heated for five hours in an oil-bath at 120—130°, and the cooled product was poured into 1·5 litres of cold water. On removal of a small part of the sulphuric acid by the gradual addition of barium carbonate to the warm solution, a point was soon reached at which crystals of the sulphonic acid began to appear. The mixture was kept until the next day, when the solid mass was filtered off and extracted with hot water. The barium sulphate was removed, and the filtrate deposited 110 grams of chloronitrobenzenesulphonic acid on cooling, the yield being more than 63 per cent. of the theoretical (Found: N = 5·37, 4·98; S = 12·12; *M* (by titration) = 272·6. $C_6H_4O_5NClS,2H_2O$ requires N = 5·12; S = 11·72 per cent.; *M* = 273·5).

In order to hydrolyse the chloronitrobenzenesulphonic acid, 15 grams of the free hydrated acid were dissolved in 50 c.c. of water and 6·8 grams of sodium hydroxide (slight excess over 3 mols.) added. After boiling for one and a half hours, and another 25 c.c. of water having been added, a deep yellow, crystalline salt was deposited on cooling. Some of the salt was lost, so that only 9 grams were collected.

The salt proved to be the disodium salt, crystallising with 2 molecules of water, described by Korner (Found: H_2O = 12·16; Na = 15·3. Calc., H_2O = 12·04; Na = 15·4 per cent.). 4-Nitrophenol-2-sulphonic acid was not examined with regard to its nitrolysis.

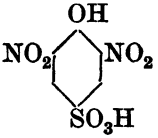
(*e*) 2 : 6-*Dinitro*-4-*sulphonic Acid.*

The first attempt to prepare salts of this acid was made by nitrating sodium phenol-4-sulphonate in concentrated sulphuric acid: a mixture of 80 grams of the crushed anhydrous salt with 160 grams of 96 per cent. sulphuric acid was cooled by ice and 58 grams of nitric acid (*d* 1·5) were run in, the temperature being kept low. Towards the end of the reaction, the temperature rose to 60° and the mixture became very pasty. On the next day the solid mass was dissolved in the minimum amount of cold water and the solution poured into a warm solution of 200 grams of crystallised sodium sulphate in 200 c.c. of water. On keeping, a pale yellow salt settled out, which was collected, and dried as completely as possible at 100°. The material was still somewhat damp and in the crude condition weighed 200 grams.

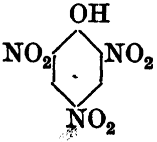
At first the salt was taken to be sodium picrate mixed with picric acid; the latter was probably present to some extent, but, as will be seen below, 2 : 6-dinitrophenol-4-sulphonic acid gives tests similar to the *iso*purpuric and picramic acid reactions. Picric acid was not present in any considerable amount, because only a green coloration was produced with ammoniacal copper sulphate, but no crystals were deposited. Further quantities of the required salt were prepared from sodium 2-nitrophenol-4-sulphonate, following the directions given by Beyer and Kegel (D.R.-P. 27271; Friedländer, "Fortschritte der Teerfarbenfabrikation," I, 324) for the preparation of the corresponding potassium salt.

The salt obtained from the strongly acid solution crystallised from a small quantity of boiling water in pale yellow plates, the yield of purified material being only 37 grams (Found: $H_2O = 15{\cdot}84$; $Na = 6{\cdot}52$, $6{\cdot}95$. $C_6H_3O_8N_2SNa,3H_2O$ requires $H_2O = 15{\cdot}88$; $Na = 6{\cdot}96$ per cent. Found: in the anhydrous salt, $S = 11{\cdot}96$. Calc., $S = 11{\cdot}19$ per cent.). It was mentioned above that the salt was at first mistaken for picric acid. The yellow plates much resemble picric acid, but are very readily soluble in water.

The ammoniacal aqueous solution gives a red colour with a solution of potassium cyanide; this was mistaken for the *iso*purpuric acid reaction, with which it evidently corresponds. The reaction is interesting as showing the equivalence of the two structures—



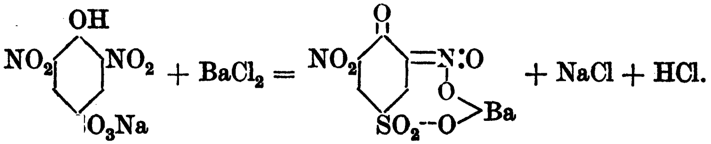
and



as far as the replacement of the hydrogen atoms in positions 3 and 5 by cyanogen and the reduction of one nitro-group are concerned.

With ammonium sulphide, the red coloration corresponding with the picramic acid reaction is only slowly produced. The distinction from sodium picrate is shown on addition of concentrated sulphuric acid to the saturated aqueous solution, no precipitate being produced. It is interesting to note that Marqueyrol and Carré (*Bull. Soc. chim.*, 1920, [iv], **27**, 127) obtained sodium 2 : 6-dinitrophenol-4-sulphonate by the further nitration of the mononitrophenol-*p*-sulphonate.

The Barium Salt.—This was obtained from the sodium salt by precipitating its solution with barium chloride solution. The precipitate was collected and crystallised from a large quantity of boiling water, in which it is somewhat sparingly soluble. It is nearly insoluble in cold water. The small, orange-red needles contain water of crystallisation and are derived by displacement of two hydrogen atoms in the acid by barium



Balentine (*Annalen*, 1880, **202**, 358) described a salt,

$$C_6H_2O_8N_2SBa,xH_2O,$$

as being nearly insoluble in water, and Bertram described a salt, $C_6H_2O_8N_2SBa,3\frac{1}{2}H_2O$, as belonging to the monoclinic system (*Jahresb.*, 1882, 368). In order to get the salt to constant weight, it was found necessary to heat it at 150°; the water content does not agree with Bertram's result (Found: $H_2O = 10{\cdot}55$; $Ba = 30{\cdot}58$.

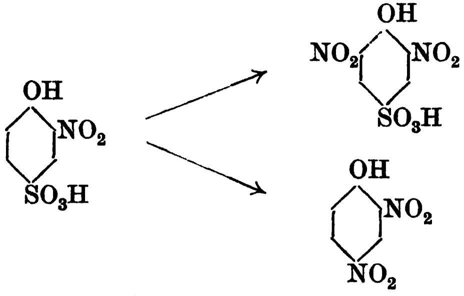
$C_6H_2O_8N_2SBa,2\frac{1}{2}H_2O$ requires $H_2O = 10{\cdot}13$; Ba = 30·92 per cent.). The anhydrous salt is crimson.

The Free Acid.—A solution of the barium salt in hot water was treated with dilute sulphuric acid until no further precipitate was formed, the barium sulphate filtered off, and the solution evaporated. After concentration to a small bulk, small, transparent crystals were deposited, which were yellow when moist, but colourless when dry. After recrystallisation, the melting point of the hydrated acid was about 111° (not sharp); the sulphur content corresponded with 2 molecules of water of crystallisation, not with 3 molecules as described by Brunnemann (*Annalen*, 1880, **202**, 348) (Found: S = 10·9; $H_2O = 11{\cdot}4$. $C_6H_3O_8N_2S,2H_2O$ requires S = 10·7; $H_2O = 12{\cdot}0$ per cent.).

The free acid gave a red coloration with ammonium sulphide on keeping for some time.

It was previously mentioned that 24 grams of material separated during the boiling of the sodium phenolsulphonate with dilute nitric and sulphuric acids. This was found to melt at 113—114°, and there was no depression when it was mixed with 2 : 4-dinitrophenol. The original, low melting point may be ascribed to admixture of picric acid.

The action of a hot diluted mixture of nitric acid and sulphuric acids on 2-nitrophenol-4-sulphonic acid may be represented by the following scheme:



When no excess of sulphuric acid is present, the second reaction predominates. Since dinitrophenol is converted into picric acid only by nitration in a mixture of concentrated sulphuric and nitric acids, it is evident that a predisposing cause of the formation of low-grade picric acid (due to admixture of dinitrophenol) is to be found in the presence of phenolmonosulphonic acid in the sulphonated mixture, and that this may be largely remedied by nitration in presence of an excess of sulphuric acid.

Continued action of dilute nitric acid on 2 : 6-dinitrophenol-4-sulphonic acid, can, however, give rise to picric acid. This explains the fact that good results have been obtained in practice when phenol has been subjected to a low initial sulphonation, but has been subsequently mixed with waste acid, that is, with a considerable excess of sulphuric acid, and subjected to a thorough after-nitration.

Under such conditions, one may expect the formation of 2 : 6-dinitrophenol-4-sulphonic acid rather than 2 : 4-dinitrophenol; the former will give picric acid with ease, whilst the latter will not

The sulpho-group is readily replaced by bromine. A solution of sodium 2 : 6-dinitrophenol-4-sulphonate was treated with bromine water in slight excess; the yellow, crystalline precipitate, after being washed and dried, melted at 76°. After recrystallisation from hot water, it melted at 77—78°.

The same compound was also obtained from the free acid and bromine water. Korner (*Jahresb.*, 1875, 339) obtained the same compound by bromination of 2 : 6-dinitrophenol and gave the m. p. as 85·6°. As there seems to be some discrepancy in the literature as to the melting point of 4-bromo-2 : 6-dinitrophenol, a specimen was prepared by the bromination and subsequent nitration of *o*-nitrophenol (Armstrong and Prevost, *Ber.*, 1874, **7**, 922). No lowering of the melting point was observed when a portion of this specimen was mixed with that produced from the dinitrophenolsulphonic acid by the addition of bromine; the orientation of the dinitrophenolsulphonic acid was thus confirmed (Marqueyrol and Carré, *Bull. Soc. chim.*, 1920, **27**, 127, give 83° as the melting point of 4-bromo-2 : 6-dinitrophenol).

An attempt to moderate the violence of the reaction, in the nitration of 4-bromo-2-nitrophenol by a mixture of sulphuric and nitric acids, was made by nitrating in the presence of acetic acid. This, however, led to the production of picric acid (the replacement of bromine by the nitro-group is worth noting).

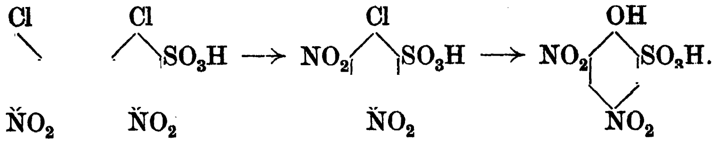
Nitration of 2 : 6-*dinitrophenol*-4-*sulphonic Acid.*

(Heating at 100° for eight hours.)

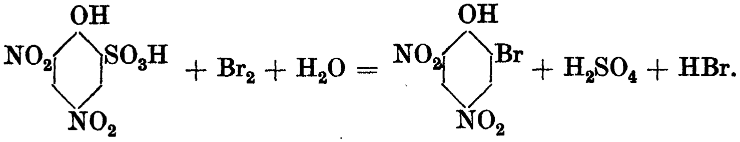
Expt.	Sodium salt (0·1 mol.). Grams.	Sulphuric acid (94 per cent.). Grams.	Water. Grams.	Nitric acid (67 per cent.; 0·21 mol.). Grams.	Yield. Grams.	Yield per cent.	M. p.
1	34	60	0	20	19	82·2	121°
2	,,	60	20	,,	19	82·8	120
3	,,	50	30	,,	21·1	91·7	120–121
4	,,	40	40	,,	20·4	88·8	120
5	,,	20	60	,,	18·4	80·3	118–119

(*f*) 4 : 6-*Dinitrophenol*-4-*sulphonic Acid.*

This acid was prepared substantially by Ullman and Herre's method (*Annalen*, 1909, **366**, 114). *p*-Chloronitrobenzene was successively sulphonated, nitrated, and hydrolysed;



The orientation of the groups was confirmed by treating the salt in aqueous solution with bromine water. The precipitate melted at 118·5°. 2-Bromo-4 : 6-dinitrophenol melts at 118·2° :



4 : 6-Dinitrophenol-2-sulphonic acid, like its isomeride, may be derived from 6-nitrophenol-2 : 4-disulphonic acid by partial nitrolysis. Marqueyrol and Carré (*Bull. Soc. chim.*, 1920, [iv], **27**, 127) have isolated this compound from the mother-liquors obtained in the manufacture of picric acid in larger quantities than the isomeride.

In a particular experiment made by the present author, the former yielded 89 per cent. of the theoretical amount of picric acid after nitrolysis at 100° for only two hours.

(*g*) 6-*Nitrophenol*-2 : 4-*disulphonic Acid.*

Although this acid must be produced from phenol-2 : 4-disulphonic acid by the action of nitric acid, it is strange that it does not seem to have been isolated from the picric acid mixture.

It was first prepared by nitrating (1 mol. of HNO_3, *d* 1·5) phenoldisulphonic acid liberated from the barium salt in presence of four times its weight of concentrated sulphuric acid, the mixture being externally cooled by ice during the process. The mixture having been diluted with four times its volume of water, barium carbonate was added, the solution boiled, and the barium salt isolated in the usual manner. The yellow salt turns red on heating at 120°, but regains its yellow colour on exposure to air after cooling. On account of the avidity with which water was absorbed, the anhydrous salt was analysed; it contains three equivalents of barium [Found : Ba = 39·9. $(C_6H_2O_8NS_2)_2Ba_3$ requires Ba = 41·0 per cent.].

For the preparation of considerable quantities of the barium salt, intermediate isolation of the phenoldisulphonic acid is unnecessary.

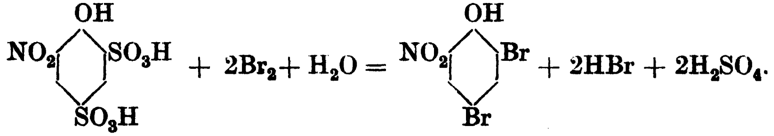
Phenol (500 grams) and 2000 grams of oleum (23 per cent.) were heated at 100° for four hours, then cooled, diluted by the addition of small pieces of ice (about 150 grams), and nitrated by the slow addition of 254 c.c. of nitric acid (*d* 1·5). The mixture was cooled externally and the temperature was not allowed to exceed 20°. The mixture, which formed a solid mass on keeping, was dissolved in 8 litres of water, neutralised with barium carbonate (about 3½ kilos.), and worked up in the manner previously described. The crude barium salt was recrystallised twice, the weight obtained being 850 grams. The salt was dehydrated before analysis (Found : Ba = 40·7 per cent.).

The Free Acid.—This may be obtained from the barium salt, but an alternative process has been worked out.

Phenoldisulphonic acid prepared from its barium salt was nitrated in the manner previously described; on keeping for some days, the nitrophenoldisulphonic acid crystallised out. It was filtered over asbestos and the adherent sulphuric acid removed by the following procedure : the solid was washed repeatedly with small quantities of ether, then dissolved in the minimum quantity of ether and a considerable excess of chloroform added. The acid was filtered off and the process repeated. As the sulphuric acid is removed, the solubility in ether diminishes.

After a third precipitation by chloroform, the acid was dissolved in water, the solution filtered, and evaporated at 100°. After some hours, crystals began to form, and concentration was then continued in a vacuum desiccator. The acid was drained on tile, and obtained as colourless, silky needles. 6-Nitrophenol-2 : 4-disulphonic acid is extremely deliquescent; the aqueous solution is pale yellow, and becomes intensely yellow on addition of alkali (Found : N = 3·88. $C_6H_5O_9NS_2,2H_2O$ requires N = 4·18 per cent. The equivalent weight, by titration, = 113·0. Calc., 111·7). Since the titration is not very easily performed, it is possible that the acid crystallises with $3H_2O$ (Calc., N = 3·96 per cent.).

Bromine water added to a solution of the free acid gave a precipitate which melted at 117° after washing and drying, and at 117·5° after recrystallisation from water. 2 : 4-Dibromo-6-nitrophenol melts at 117·5° (Arzruni, *Jahresb.*, 1877, 548) :



Formation of 2 : 4-*Dinitrophenol.*

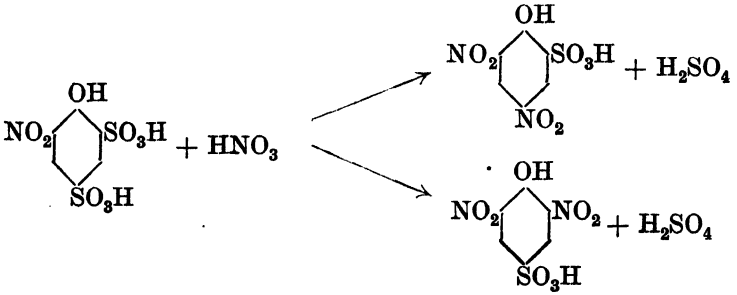
It has been pointed out that dinitrophenol is formed by nitrolysis of 2-nitrophenol-4-sulphonic acid. The latter compound probably owes its origin as a general rule to phenol-4-sulphonic acid (low degree of sulphonation).

Nitrolysis of Sulpho-groups in the ortho- *and* para-*Positions.*

It was stated in the introduction that a sulpho-group is more readily displaced by the nitro-group from position 4 than from position 2. This is shown by the following experiment. It was thought advisable to avoid complications due to replacement of hydrogen in the nucleus, and therefore 6-nitrophenol-2 : 4-disulphonic acid was selected for the experiment.

The trisodium salt (77·5 grams; 0·2 mol.), containing 5·86 per cent. of moisture, was finely crushed, mixed with 68·6 grams of sulphuric acid (96 per cent.), the mixture was diluted with its own volume of water, and heated for two hours at 100° with 22·84 grams of nitric acid (69 per cent.; 1·25 mols.). The reaction was not violent, brown fumes were evolved, and, on cooling, the whole mass solidified; 54 grams of material were isolated. The major portion was separated into three fractions. The first (7 grams) consisted essentially of picric acid, the second (2·5 grams) also contained picric acid and was neglected. The main crop (32 grams) was fractionally crystallised; the four crops obtained, when treated with bromine, gave brown compounds with melting points varying from 113° to 118°. No depression of melting point was observed on admixture with a specimen of 2-bromo-4 : 6-dinitrophenol (m. p. 118·2°); the bromo-compound must then have been produced from 4 : 6-dinitrophenol-2-sulphonic acid. Care must be taken that bromine is not added in large excess to the dinitrophenolsulphonate; Marqueyrol and Carré (*loc. cit.*) have shown that under this condition 4 : 6-dinitrophenol-2-sulphonic acid gives rise to 4-bromo-2 : 6-dinitrophenol to a large extent.

Thus of the two initial reactions between 6-nitrophenol-2 : 4-disulphonic acid and nitric acid,



the first must be preferred, even if it does not take place exclusively. Confirmatory evidence was afforded by heating 2 : 6-dinitrophenol-4-sulphonic acid and 4 : 6-dinitrophenol-2-sulphonic acid under similar conditions with a mixture of water and nitric and sulphuric acids. Reaction began immediately with the first of these acids, but was not evident with the second acid during the first half-hour. After being heated for two hours, the first mixture gave a yield of 91·7 per cent. of picric acid, and the second a yield of 81·6 per cent.

Formation of Oxalic Acid.

The quantity of oxalic acid produced during the nitration of:

A. Sodium phenol-4-sulphonate, $C_6H_5O_4SNa,2H_2O$,

B. Sodium 2-nitrophenol-4-sulphonate, $C_6H_4O_6NSNa,3H_2O$,

and

C. Sodium 2 : 6-dinitrophenol-4-sulphonate, $C_6H_3O_8N_2SNa,3H_2O$,

was determined under varying conditions. The formulæ indicate the form in which the material was weighed. The salt was dissolved in water, the solution made up to a definite volume, and an aliquot portion was rendered alkaline with ammonia and precipitated with calcium chloride. The precipitate of calcium sulphate and oxalate was washed free of picric acid, and the oxalic acid estimated by permanganate.

	Weight in grams of reagents employed in the nitration of 1 gram-mol. of the salt.			Grams of oxalic acid produced from 1 gram-mol. of the salt.
	94% H_2SO_4.	Water.	67% HNO_3.	
A	596	0	399	12·35
A	366	400	405	14·21
B	612	0	300	4·67
B	605	200	304	3·77
B	507	300	306	10·49
B	448	400	295	10·41
B	200	600	300	14·15
C	600	0	200	2·18
C	600	200	200	0·45
C	391	391	200	0·91
C	200	600	200	0·34

The table shows that the introduction of the nitro-group into the phenolsulphonate before dilution and further nitration to picric acid increases the stability.

The foregoing work was carried out at H.M. Chiswick Laboratory, Department of Explosives Supply, in 1917—1918, and is now published with permission of the Director of Staff Duties.

The author wishes to thank Dr. J. T. Hewitt, F.R.S., formerly Director of the Chiswick Laboratory, for his advice given throughout the course of this work.

University College,
Exeter.

[*Received, November* 17*th*, 1921.]

OBITUARY NOTICES.

ALBERT ERNEST BELLARS.

BORN AUGUST 25TH, 1880; DIED APRIL 23RD, 1921.

ALBERT ERNEST BELLARS was the son of the late Alderman E. B. Bellars of Wisbech. He was educated at Wisbech Grammar School under Mr. A. W. Poyser and at Magdalene College, Cambridge, where he held a Holmes Exhibition. After taking his degree in the Natural Sciences Tripos in 1902, he was appointed Assistant Demonstrator in the laboratory of Gonville and Caius College under Mr. M. Pattison Muir. Later he undertook the supervision in chemistry of students in Gonville and Caius and in Magdalene Colleges. Between 1903 and 1910 he was engaged in research work, the results of which have appeared in the *Transactions of the Chemical Society* and in the *Proceedings of the Cambridge Philosophical Society*. At Cambridge he was an enthusiastic teacher and very popular with students in the laboratory and in the college classes under his supervision. As a colleague in research, he was a skilful and accurate experimenter, and he never tired in his determination to solve a problem. No failure disheartened him, and his cheery optimism gave stimulus to work in which he was engaged. With the writer he published between 1903 and 1907 the results of four investigations which have appeared in the *Transactions*. In 1911, after the closing of the chemical laboratory of Gonville and Caius College, he was appointed Professor of Chemistry at the Rangoon University College on the recommendation of Sir W. J. Pope, and soon proved himself to be a stimulating lecturer and teacher. Last year he was appointed the first Professor of Chemistry in the new University of Rangoon.

The splendidly-equipped chemical laboratory at University College is a monument to his thoroughness and foresight, and a long list of those who have graduated in science in Burma during the last ten years bears testimony to his unwearying labour and to the activity of the interest in that branch of science of which he himself was so keen a student. The claims of teaching work left little opportunity for research until lately, when in the new laboratory he was able to resume it. Serious throat trouble compelled him to come to England this year for an operation, which was at first successful, but a sudden attack of hæmorrhage occurred later, which was fatal. In December, 1919, Professor Bellars married Miss Beryl Coxon, only daughter of Major Coxon, of King's Lynn, Norfolk. She returned to England with her husband this year and was with him at his death. Professor Bellars leaves a posthumous son born a week after his death. In Burma, great sympathy is felt for his widow, who had been in the colony only a little more than a year when her husband was invalided home. Bellars was a keen sportsman in every sense of the word. At Cambridge he was captain of his college cricket team and played regularly in the Cambridge County Eleven. He was an enthusiastic skater of the fen style and a golfer. In the Long Vacations he was one of the band of climbers of the Alpine Club and was associated with the late Dr. H. O. Jones in several of his ascents. In the Easter Vacations he climbed in Snowdonia or in the Lake District. While in Rangoon he took a keen interest in all matters connected with sport and volunteering at the University College and officiated regularly at the local athletic meetings.

His sudden and early death is much to be deplored. Bellars was the ideal type of colonial University Professor. The soundness of the knowledge of his subject combined with a driving power and personality commanded the loyalty and respect of his students, not only in the lecture room, but also in the college sports. He was of the true type of teacher and leader of men, such as have built up the British Empire, and yet he was of a retiring disposition and never sought popularity outside the circle in which his main interests lay. He was devoted to his work and to his home.

R. S. MORRELL.

EDWARD JOHN BEVAN.

BORN DECEMBER 11TH, 1856; DIED OCTOBER 17TH, 1921.

EDWARD JOHN BEVAN, son of Edward Bevan, of Birkenhead, was born in 1856. After a private school education he received a training in chemical science which may be described as irregular.

Beginning at the age of seventeen with the routine of laboratory control of alkali processes in the service of the Runcorn Soap and Alkali Co., he made friendships with certain pioneer workers in that industry, who usefully influenced his career by advising systematic training at the Owens College—then a leading centre of research. The meeting with C. F. Cross resulted in a student friendship which developed into one of collaboration, both leaving the College (1879) to undertake research work in the cellulose industry, Bevan's sphere being that of paper-making. Problems of common interest were investigated, of which results were published in the *Journal of the Chemical Society* (1882). It was already evident that the field of work entered on, promised results in proportion to industry; it was decided to make a definite adventure, and "Cross and Bevan," migrating to London, were able to find a provisional working home in the Jodrell Laboratory, Kew, through the friendly offices of H. E. Armstrong, Hugo Müller, and Thiselton-Dyer.

The scope of research widened to include the physiology of the vegetable fibres, the equilibrium of the fibre substances as chemical individuals in relation to water-oxygen conditions, hence a special study of cellulose reactions with hydrolytic agents and oxidants; and in development of the natural history aspect of the subject, the working out of a comprehensive scheme of analysis of the fibres and fibre-aggregates, the raw materials of the textile and paper-making industries.

The scientific data thus accumulated were then applied in developing industrial inventions, such as the bisulphite process of treating wood for the preparation of cellulose ("pulp"), then in its infancy, and pioneered in this country by C. D. Ekman: and textile bleaching processes, for example, those of Thompson, Hermite (electrolytic), and W. Mather. The Colonial and Indian Exhibition provided a sphere of active work in vegetable fibres, and established the method of analysis and evaluation of these raw materials as a "standard," subsequently to be generally accepted as such. Concurrently with these technical activities, the systematic research work on cellulose and its derivatives was followed up and investigations of alkali-cellulose (mercerisation) and benzoates (Baumann's method) led in logical sequence to the discovery of the xanthogenic hydrate-ester series of derivatives, patented in the joint names, and the basis of the now well-known "viscose" industries.

The formal partnership "Cross and Bevan," and its establishment at New Court, Lincoln's Inn (1885), led to outside activities, such as those connected with patent litigation, in which Bevan showed his exceptional abilities, and decided leanings to the professional side of chemical science. Applying for the post of Public Analyst under the Middlesex County Council, he was appointed (1892), and held the office to the date of his death. As necessary incidents of this position, he became progressively influential in the Society of Public Analysts, of which he was sometime President, and on the Council of the Institute, devoting himself with his usual thoroughness to its interests and high aims.

Bevan's career expresses his whole-hearted devotion to Science, for his varied activities were all marked and hall-marked by the severe discipline of the pursuit of "the Truth" as "the whole Truth and nothing but the Truth," as we chemists know the truth of an experimental science, with the uncompromising laws under which we work for its establishment.

With these qualities were associated those which express themselves in good fellowship. Bevan was popular, as he was genial and generous. His surviving relatives treasure the many expressions of affection and regard contained in letters from his brother chemists.

For a complete and chronological record of the publications in which Bevan was associated with the writer, those who may be interested are referred to the *Paper Trade Review* of January 28th, 1921.

C. F. CROSS.

EDWARD KINCH.

BORN AUGUST 19TH, 1848; DIED AUGUST 6TH, 1920.

EDWARD KINCH was born at Henley-on-Thames, and was educated at the Grammar School there. His father, Charles Kinch, was a pharmaceutical chemist, and would seem to have been a very energetic man, for he also had a printing and stationery business, published a local paper, and took an active part in the management of the affairs of the town.

Although Edward Kinch spent his early life there, it is not in association with Henley that one thinks of him, but with that agricultural district on the Upper Thames where the counties Berkshire, Wiltshire, Oxfordshire, and Gloucestershire meet. There on the Berkshire bank of the Thames lies the scattered village of Eaton Hastings, and at the "Grange," a charmingly old-fashioned, somewhat rambling farmhouse, many generations of the Kinch family had dwelt and farmed their own land, whilst relations of theirs were to be found in many of the large farms in the district lying between Farringdon and the Cotswolds. Amongst them were men who have made their mark in agriculture, such as Charles Hobbs of Maisey Hampton and his son Robert Hobbs of Kelmscott, both so well known as successful breeders of sheep. It may be mentioned incidentally that the picturesque Manor House at Kelmscott, standing opposite to Eaton Hastings on the Oxford bank of the Thames, which figures so much in the art annals of the Victorian era as the home of William Morris, and for a time also of D. G. Rossetti, belonged to a widowed aunt of Edward Kinch who lived with her brother William at the Grange. It was in his frequent visits to these relations probably that Edward Kinch acquired that interest in agriculture that became the dominant feature in his life.

On leaving school, Kinch went to the Royal College of Chemistry in Oxford Street, where he studied for some years under Prof. (later Sir Edward) Frankland. His first appointment (1869) was that of chief assistant to Prof. (later Sir Arthur) Church at the Royal Agricultural College, Cirencester, and thus began the connexion with the institution with which later he was so intimately associated. He held this post until the latter part of 1872; he then joined the staff of the Royal College of Chemistry, which, with some sections of the Royal School of Mines, had just been transferred to the new buildings in the Exhibition Road, South Kensington, to form the nucleus of that institution which after many changes of name is now known as the Imperial College of Science and Technology. After some years spent in teaching in these laboratories, Kinch for about a year held the position of Superintendent of Minerals at the India Museum, South Kensington. In 1876 he accepted the post of Professor of Chemistry at the Imperial College of Agriculture, Komaba, Tōkyō, Japan, in the organisation of which he took an active part. At this time Japan was still in large part closed to Europeans, but in the college vacations Kinch was allowed to travel freely about the country, and had opportunities such as fell to few others of seeing "Old Japan." One considerable drawback, however, was that in many of the out-of-the-way districts it was impossible to supplement in any way the meagre vegetable diet of the natives—the result to a European being semi-starvation.

In 1881, Kinch returned to England on his appointment as Professor of Chemistry at the Royal College of Agriculture, Cirencester, a post which he held until the closing down of the College in 1915 on account of the war.

Prof. Kinch married, in 1889, Edith, daughter of the Rev. George Huntingdon, vicar of Tenby, but their happy married life was terminated by her death a year later.

On the closing of the Cirencester College, Kinch retired from active life and went to live at Haslemere, where he occupied himself with his garden, and with Japanese art, a subject in which he was greatly interested. His residence in Japan had enabled him to form a small but admirable collection of curiosities and art work. A serious illness in 1918 left him with very impaired health, and he died on August 6th, 1920.

Edward Kinch was a man who devoted himself heart and soul to his students and to the interests of the Royal Agricultural College, Cirencester, where he spent thirty-four years of his life. Singularly unassuming, and of very retiring nature, he was beloved by those who came under his influence, and the fruits of his sound and careful training of his students were manifested by many of them in subsequent spheres. It was for his college and his students that he lived, and it was in this connexion, rather than in public life, or in written contributions to science, that he excelled. His principal literary contribution was the revision and practical re-writing, in 1906, of the well-known book for agricultural students, "Church's Laboratory Guide," of which a ninth edition appeared in 1912. Occasional papers from him have also appeared in the *Journals* of the Chemical Society, the Royal Agricultural Society, and the Surveyors' Institute, but most of his contributions were given in the *Agricultural Students' Gazette*, issued from the Cirencester College. Kinch was a sound, rather than a progressive, chemist, and a teacher, rather than an investigator, but he was a man held in much esteem by those who knew him. In conclusion, the words of a former student, Lord Bledisloe, intimately acquainted with the affairs of the College, may be quoted: "If and when the worthy history of England's premier agricultural college comes to be written, no name will rank higher in its annals than that of Edward Kinch, and no one will be deemed to have wrought a more beneficial influence in promoting the high reputation of the College and the progress of Agricultural Science in the British Empire."

Prof. Kinch served on the Council of the Chemical Society, 1887—1892; at an earlier period, 1872—1875, he was on the Journal staff as an abstractor in Agricultural Chemistry. A. J. G.

HENRY RONDEL LE SUEUR.

BORN JANUARY 1ST, 1872; DIED JULY 9TH, 1921.

H. R. LE SUEUR was born at Trinity, Jersey, on January 1st, 1872, the son of F. C. Le Sueur. He was at a private school until 1887, after which he spent two years in the laboratory of a Jersey analyst, Mr. F. W. Toms, and then entered University College, London, taking the Honours Chemistry course. He graduated B.Sc. of London University in 1893 and obtained the D.Sc. degree in 1901. He was a Fellow of the Institute of Chemistry (Associate 1898) and a member of its Council from 1914 to 1917: a Fellow of this Society (1895), a member of Council (1907–1911), and at the time of his death was one of its Secretaries.

After graduating in 1893, Le Sueur spent one year in carrying out research work on the properties of dehydracetic acid (Collie and Le Sueur, T., 1894, **65**, 254), and in the following year took up a junior teaching post in the Medical School of St. Thomas's Hospital. Possessing the faculty of imparting knowledge to others, Le Sueur rapidly developed into a teacher of the very first order, and it is a remarkable fact that one possessing such pronounced capabilities in this direction should have remained attached to this one Institution for the twenty-seven years of his career. The writer is well acquainted with the happy atmosphere of St. Thomas's, and no doubt this weighed with Le Sueur, especially as from 1904 he occupied the senior teaching post, but it is none the less strange that his exceptional teaching capacity was not more generally recognised.

There was only one break in the twenty-seven years during which Le Sueur was connected with St. Thomas's, namely, that caused by the War. He was gazetted major, Royal Engineers, in 1915 and with Major J. T. Hewitt was ordered to Gallipoli to watch and advise on possible developments in gas warfare. There can be little doubt that the illness which he contracted there seriously undermined his health, for he was never in reality the same high-spirited man again. On his return to England, after being in hospital in Egypt, he became one of the chief experimental officers at the R.E. Experimental Station, Porton, where he was attached until the end of 1917. He was then ordered to the United States to assist in the preparation of the American Gas Warfare Experimental Station, and he remained there until after the signing of the Armistice.

As a research worker, Le Sueur was not prolific, his total published papers amounting to twenty-four; this is largely accounted for by the fact that research was regarded by him as a pleasurable relaxation from his teaching duties, which always came first. He thoroughly enjoyed every minute he was able to devote to experimental work, but when accumulated results made the writing of a paper desirable he was very obviously bored. His researches concerned mainly the fatty acids and their hydroxylated derivatives, and may be divided into three groups. In one, he studied the action of heat on the α-hydroxycarboxylic acids and showed that it is possible to descend the series of fatty acids, step by step, according to the scheme, $R\cdot CH_2\cdot CO_2H \longrightarrow R\cdot CHBr\cdot CO_2H \longrightarrow R\cdot CH(OH)\cdot CO_2H \longrightarrow R\cdot CHO \longrightarrow R\cdot CO_2H$. A somewhat similar process led, in a second series of experiments, to a simple method for the preparation of secondary amines, thus: $R\cdot CHBr\cdot CO_2H \longrightarrow R\cdot CH(NHAr)\cdot CO_2H \longrightarrow R\cdot CH_2\cdot NHAr + CO_2$, whilst the third group of researches, on the action of fused potassium hydroxide on the dihydroxy-acids obtained by oxidation in the oleic acid series, revealed an unusual transformation, namely, the movement of a heavy radicle within the molecule of an aliphatic compound. The change is represented thus: $R{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_n{\cdot}CO_2H \longrightarrow OH{\cdot}CH_2{\cdot}CR(OH){\cdot}[CH_2]_n{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CR(OH){\cdot}[CH_2]_n{\cdot}CO_2H$. The elucidation of the constitution of the hydroxydicarboxylic acids formed in this way led, incidentally, to the discovery of heneicosoic acid, a missing member of the simple fatty acid series.

In manner Le Sueur was quiet and reserved, not to say shy; few knew him well, for his efforts to disguise the above characteristics sometimes gave quite a wrong impression of the real man. His great outstanding quality was loyalty, which governed his every action and was one of the main causes of the loving regard in which he was held by his intimate friends. As a Jerseyman, Le Sueur had an intense feeling of local patriotism, and his friends knew well his loyalty to the "Duke of Normandy." He was one of the founders of the Jersey Society in London and one of its most active members during more than twenty years, being chairman of its council at his death. He spoke a dialect of the ancient Norman-French language fluently and with historical pride, and it was because of his love for his native land that he desired to be laid to rest in Jersey.

A. W. CROSSLEY.

GEORGE BLUNDELL LONGSTAFF, M.A., M.D. (OXON.), F.R.C.P., F.S.A., F.L.S., F.C.S., F.G.S., J.P.

BORN FEBRUARY 12TH, 1849; DIED MAY 7TH, 1921.

IN the late George Blundell Longstaff the scientific, the artistic, and the practical temperaments were so nicely blended that it would be impossible to say which of these qualities preponderated in his attractive and versatile nature. Those who made his acquaintance as a field naturalist and had occasion to note his keen powers of observation, his untiring activity as a collector, and his readiness to appreciate the scientific bearing of the facts that he and others accumulated, might not unnaturally be surprised to find that his technical knowledge of the building craft was the admiration of experts, and that his judgment on all matters of the graphic and plastic arts was highly valued by the most experienced critics.

It is interesting to call to mind that many of the most conspicuous traits in Longstaff's character may be traced back to his ancestry. Thus his father, in early days an associate of "Osmotic Graham," was noted for his devotion to chemistry; to the Dixon strain may be attributed his interest in everything practical and constructive; while the extraordinary energy with which he worked at entomology may be considered not improbably to be foreshadowed in the stock from which sprang Spence of "Kirby and Spence."

Born at Wandsworth in 1849, Longstaff was the second son of Dr. George Dixon Longstaff, and of Maria, daughter of H. Blundell, of Hull. At Rugby he came under the influence of Archbishop Temple, then Headmaster, and of Archdeacon J. M. Wilson, then Master in Natural Science and Mathematics. Each of these great teachers left a strong impress on the mind and character of their pupil. Proceeding in due course to Oxford, he gained a scholarship in Natural Science at New College, following this up with a First Class in Natural Science. It was while an undergraduate at Oxford that by a deplorable accident he lost the sight of an eye. Throughout his life the condition of his sight was such as to necessitate the greatest care in the use of his remaining eye; and he was compelled to forego many schemes of scientific research which his inclinations would have led him to adopt. But he faced his misfortune with admirable courage, and engaged with vigour and energy in all the pursuits of a kindred nature which still remained open to him. After taking his degree in Arts, he entered at St. Thomas's Hospital, and having passed through his career as a medical student with distinction, he graduated as M.B., subsequently as M.D., at Oxford; and obtained the Membership, eventually the Fellowship, of the Royal College of Physicians. In 1875 he married a daughter of Edward Dixon, of Southampton, a member of a family already connected with his own. The intellectual endowments, the philanthropic ideals, and fine taste of this lady were most congenial to him, and it would have been difficult to find a better-assorted couple. On settling down with his wife and young family, first at Wandsworth and afterwards on Putney Heath, he devoted himself to the study of preventive medicine and vital statistics, paying special attention to all such matters as might benefit the conditions of life among the poorer and less fortunate members of the community. The present writer became associated with him in some of this early work, especially in the investigation of the properties of a much-advertised germicide, and in the statistical aspects of various diseases. This led to a long collaboration in the Registrar-General's Department at Somerset House, many results of which saw the light in his published volume of "Studies in Statistics." Whilst still engaged in work of this kind, he acquired the beautiful estate at Mortehoe, in North Devon, where much of his subsequent life was passed, and where he threw himself with characteristic energy into the study of the history, antiquities, natural productions, and social conditions of that part of the county. To these rural pursuits he added much varied activity in London, serving on the London County Council as member for Wandsworth from 1889 to 1903; and, as Chairman of the Building Act Committee of that body, taking a principal part in the drafting and passing through Parliament of the London Building Act, 1894. As J.P. both for London and Devon, he gave much time to magisterial duties, and as Guardian of the Poor he found scope for the exercise of his interest in the social conditions of the more indigent classes.

It had always been his desire to travel; and he soon found opportunity to acquaint himself with many remote parts of the earth. At different times he visited Madeira, the Canary Islands, Algeria, Egypt and the Soudan, South Africa, India, Ceylon, China, Japan, North and South America, the West Indies, Australia, and New Zealand. In all of these places he made large collections, principally of insects, and recorded numerous observations of high interest in the elucidation of bionomic questions. The results of these labours in the field of natural history were published by him in several important memoirs, collected some nine years ago in a volume entitled "Butterfly Hunting in Many Lands." The insect collections, which are of great value both in themselves and for the exact data by which each specimen is accompanied, were presented by him to the Hope Department in the University of Oxford. This Department found in him a generous and far-sighted benefactor; it being indebted to him, amongst other donations, for an endowment of £2400 for the provision of an additional assistant. Beside all his other avocations, he found time to take an active part in the work of the Charity Organisation, the Royal Statistical and the Entomological Societies, being at various times Vice-President of the latter two. He was also a Fellow of the Linnean and Geological Societies, of the Society of Arts, and of the Chemical Society. In the last-named he took a special interest, and in the year 1916, to mark the seventy-fifth anniversary of the Society, he made over to it the sum of £1000 for its Research Fund; thus following the example of his father, who in 1876 had given £1000 to establish this Fund. A "Longstaff Medal" is awarded by the Council of the Society every three years for the best series of original investigations in chemistry published in England. Longstaff's munificence was not confined to scientific objects; for many schemes of social improvement were helped by him with ample donations, and he was a liberal benefactor to the Church. He was especially concerned in the planning and building of the new church at Woolacombe, North Devon; and the ancient church of Mortehoe bears many marks of his generosity; in particular, a beautiful stained-glass window by his friend Selwyn Image, lately Slade Professor of Fine Art at Oxford.

Three years after the death of his first wife he married Miss Donald, a daughter of the late M. H. Donald of Stanwix and Blaithwaite, Co. Cumberland, a lady distinguished for her attainments in conchological science, and with many interests similar to those of her husband.

A man of such varied capacities and of so generous and sympathetic a nature as George Blundell Longstaff was sure to have numbers of attached friends, by whom his death is felt as a grievous personal loss. His memory will be widely cherished as that of an inspiring and stimulating companion, and one of the most considerate and open-handed benefactors of his generation.

F. A. D.

EDMUND JAMES MILLS.

BORN DECEMBER 8TH, 1840; DIED APRIL 21ST, 1921.

PROF. E. J. MILLS, who died on April 21st, 1921, was born in London on December 8th, 1840. He was educated first at the Grammar School, Cheltenham, and then at the Royal School of Mines, where he took the courses of instruction for a degree in science at London University, at that time the only university in Britain granting such degrees. He graduated B.Sc. in 1863, and obtained the doctorate in 1865. There were few candidates for science degrees at that time, and on looking at the list of graduates it is interesting to note that Mills's name appears about equidistant in time between those of Prof. Alex. Crum Brown, in 1862, and Sir William Tilden, in 1871.

In 1861, Mills became assistant to Dr. John Stenhouse, and a year later he was appointed one of the demonstrators in chemistry at Glasgow University, in which capacity he conducted tutorial classes for medical students, a work not very congenial to him, and one for which, from his temperament, he was not particularly well fitted; he was, however, a good laboratory teacher for advanced students. He resigned this appointment in 1865. In 1875 Mills became superintendent of the "Young Laboratory," in Anderson's College, Glasgow, and during his term of office, about the year 1886, that foundation together with Anderson's College, became incorporated in the Glasgow and West of Scotland Technical College, the Young Laboratory appointment being converted into the Young Chair of Technical Chemistry. His predecessors in charge of the Young Laboratory were W. H. Perkin, sen., 1870–71, and G. Bischof, 1871–75.

Mills was the author of many papers covering a wide field of work. Although his first recorded paper in the *Proceedings of the Royal Society* (1860) is upon bromo- and chloro-phenylamine, his early work inclined more to general and inorganic chemistry, dealing with subjects such as isomerism, statical and dynamical ideas on chemistry, chemical equivalents, etc., and this tendency is seen also in his later papers in the *Philosophical Magazine*, published during 1883, 1884, and 1887. In the *Journal of the Chemical Society* his more important papers are :—"On Aniline Derivatives and Nitrotoluene" (1875–76); "On Potable Waters" (1878–81); "On Chemical Repulsion" (1880–81); "Melting-points" (1882). From 1879 to 1882 he published "Researches on Chemical Equivalence"; from 1878 to 1880 papers on "The Action of Oxides on Salts"; and later, "Researches on Dyeing," in conjunction with Louis Campbell. To the Society of Chemical Industry he contributed papers on the "Quantitative Estimation of Oils and Fats" (1883), "Viscosity Determinations" (1886), and "Oxidation of Aniline" (1894). In his books, Mills did not confine himself to purely scientific matters; for, in addition to two works, "Fuel and its Applications" (published conjointly with E. J. Rowan in 1889) and "Destructive Distillation" (1892), he wrote a volume of poems, "My Only Child" (1895), and "The Secret of Petrarch" (1904).

Mills was elected a Fellow of the Royal Society in 1874, and was an honorary LL.D. of Glasgow University; he was an original member of the Society of Chemical Industry and served on the committee of the Glasgow Section, including two periods as vice-chairman, from 1884 to 1894; and was a member of the Council of the Chemical Society at various times from 1868 to 1906, serving as vice-president from 1912 to 1915.

Mills returned to London, finally settling at West Acton. He spent much of his leisure time in the practice of photography, in which he was a skilled manipulator. He attended many of the meetings of the Scientific Societies to which he belonged, and rendered valuable service to the Chemical Society as a member of the Library Committee, in which he took special interest.

J. M. T.

RICHARD HENRY VERNON.

BORN JANUARY 27TH, 1885; DIED APRIL 9TH, 1921.

RICHARD HENRY VERNON was the elder son of the late Hon. William Vernon, son of the sixth Baron Vernon, and of Mrs. Vernon, daughter of the late General Daniel Marsh Frost, of St. Louis City, U.S.A.

Born in London at 12 Clarges Street, Vernon had a serious illness at the age of nine which left consequences that made it doubtful whether he would be able to stand the English climate. He was therefore educated in Switzerland. He entered the École Cantonale at Lausanne in 1898 and proceeded to the Gymnase Scientifique, which he left with the Certificat de Maturité in 1902. Here he showed powers of work and a capacity for scientific and mathematical subjects which won the highest opinion from his teachers.

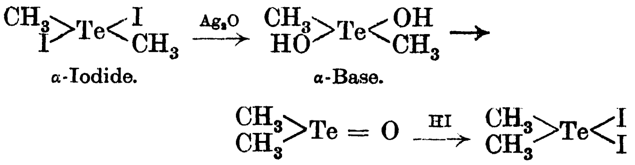
It had always been his father's desire that he should receive an American University education, and at the age of nineteen he entered at Cornell. He was then full of high spirits and love of adventure, and it was there that he won a bet that he would walk sixty miles in twenty-four hours. He covered the distance with two hours to spare, although it was in winter and the walk had to be made in the snow. However, he found the environment at Cornell uncongenial. The free open-air life of the Western States had an irresistible attraction for him, and to the concern of his parents he broke off his University career and went to California, where a maternal uncle had an estate. Here he learnt all the craft of the ranch—afterwards at Cambridge he would sometimes amuse his friends by illustrating with a rope some of the skill that he had acquired with the lariat—and for some time he lived an independent life, maintaining himself as "broncho-buster" and cowboy. Drifting in this way from California to Texas, he came at length to the little township of Throgmorton. Here there was a schoolmaster who had some knowledge of physics and with him Vernon became very friendly. The two used to discuss scientific problems together, and Vernon was made by him to realise that he had gifts which were being wasted in the life he was then leading, and was persuaded to return to Europe to continue his education. His parents were at Wiesbaden, and he joined them there and spent six months working in the laboratory of Professor Fresenius. Fresenius recognised his ability and encouraged him to take up chemistry as a profession. Accordingly, in 1907, at the age of twenty-one, he entered the Eidgenössische Technische Hochschule at Zurich, where, after working through the customary four years' course in chemistry, physics, and mathematics, he obtained the diploma in 1911. He then began, under the direction of Prof. F. P. Treadwell, the work on the electric conductivity of very pure water which was to form the subject of his thesis for the doctor's degree. The greater part of this thesis is occupied with the calculation of the relations between the inductances and capacities of the arms of the Wheatstone bridge which give the sharpest minimum of sound in the telephone. He demonstrated the practical utility of arrangements based on his results, and employed them to examine the methods of obtaining pure water by distillation. After receiving his doctor's degree in the spring of 1914, he began a magneto-chemical investigation of platinum compounds with Prof. Pierre Weiss, but this was cut short by the events of the following August. He was then fishing in the Black Forest and barely succeeded in crossing the frontier at the declaration of war. He hastened to England to offer his services, but was rejected several times on account of eyesight. Ultimately he enlisted in the R.A.M.C., but after serving for a short time with that corps he was transferred to the Royal Engineers, where he became a despatch rider. In 1915 he was granted a commission in the 3rd Battn. of the Dorset Regiment, and in the spring of 1916 proceeded to the Western Front, where he saw much active service, chiefly in the Armentières district and on the Somme. After two long periods of illness in hospital he was pronounced unfit for active service and was transferred for duty to the Chemical Warfare Committee, for whom he worked, first at the Imperial College of Science in conjunction with Prof. Baker on dichlorodiethyl sulphide, and afterwards at Cambridge in the University Chemical Laboratory, where, at the suggestion of Sir William Pope, he began an investigation of the alkyl tellurium compounds.

In July, 1918, Vernon was sent as Chemical Adviser to the Shell Filling Factory at Chittening. Here he rendered services of the greatest value in contriving precautions to be taken in the handling of "mustard gas," in working out methods for cleaning up spills and rendering the waste innocuous, and in training the operatives in the use of the measures which had been devised. It fell to him to grapple with the mischances that not infrequently occurred. When, for example, as happened in the early days of the factory, a defective cock led to a spill of several gallons, it was the Chemical Adviser who had to deal with the emergency. He won the regard and confidence both of the staff and of the operatives; the men of his special anti-gas detachment in particular gave him willing and loyal support. Life in the factory at first was rendered intolerable by the vapour of the "mustard gas," which permeated everything; sometimes, in fact, before the later improvements were introduced.

the whole of the workers in a shed would be left on the sick list at the end of a four hours' shift. It was largely through the devotion, and indeed the heroism, of the Chemical Adviser that in spite of everything the factory was able to send out in a steadily increasing stream the shells so urgently needed to enable the troops in the field to reply to the deadly weapon which the enemy had adopted.

By the continuous strain of work such as this Vernon's health was severely tried and at the time of the Armistice he was in hospital very dangerously ill with pneumonia. After a period of convalescence in the south of France he was able to return to Cambridge, and in the spring of 1919 he entered Gonville and Caius College as a research student and resumed his work on the tellurium compounds.

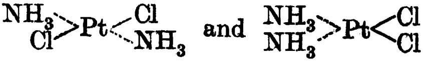
Before going to Chittening Vernon had prepared a number of dimethyltelluronium derivatives. He now examined more closely the base formed by treating dimethyltelluronium iodide in aqueous solution with silver oxide, and thus made the highly interesting discovery that when the solution of this base is evaporated to dryness a new base is produced, the salts of which are isomeric with those of the original series. As a difference of structure seems excluded, the two series of salts are almost certainly stereoisomeric. Vernon's observations indicate therefore that in dimethyltelluronium iodide the four radicles about the tellurium atom have not a regular tetrahedral arrangement as might have been anticipated, but lie more or less in one plane.



$$\underset{\alpha\text{-Iodide.}}{\mathrm{\substack{CH_3\\ I}\!>\!Te\!<\!\substack{I\\ CH_3}}} \xrightarrow{\mathrm{Ag_2O}} \underset{\alpha\text{-Base.}}{\mathrm{\substack{CH_3\\ HO}\!>\!Te\!<\!\substack{OH\\ CH_3}}} \longrightarrow$$

$$\underset{\beta\text{-Base.}}{\mathrm{\substack{CH_3\\ CH_3}\!>\!Te=O}} \xrightarrow{\mathrm{HI}} \underset{\beta\text{-Iodide.}}{\mathrm{\substack{CH_3\\ CH_3}\!>\!Te\!<\!\substack{I\\ I}}}$$

According to this view the α-salts and α-base are *trans*-compounds, the β-salts are *cis*-compounds, and the displacement of the methyl groups on heating the α-base is due to the fact (for which some experimental evidence was obtained) that the β-base is an oxide. The marked analogy which this formulation indicates between the configurations of the dimethyltelluronium iodides and those of platosamminochloride and platosemidiamminochloride as interpreted by Werner is very suggestive.



$$\mathrm{\substack{NH_3\\ Cl}\!>\!Pt\!<\!\substack{Cl\\ NH_3}} \quad \text{and} \quad \mathrm{\substack{NH_3\\ NH_3}\!>\!Pt\!<\!\substack{Cl\\ Cl}}$$

This work, the results of which are published in four papers in the Society's *Transactions* (T., 1920, **117**, 86, 889; this vol., p. 105, 687), occupied Vernon until Christmas. For it he was awarded the certificate of research of the University and in due course took his B.A. degree.

During the Christmas vacation, which he spent at Montreux, he was attacked with another serious illness, and in consequence had to undergo a severe abdominal operation, so that he was unable to return to Cambridge until Easter, 1920. He was then appointed to the official position in the University of Assistant to the Professor of Chemistry and began, in conjunction with Sir William Pope and Mr. F. G. Mann, a detailed experimental investigation of the interaction of ethylene and sulphur monochloride (this vol., p. 634). During the next few months his health, to external appearances, improved greatly, and he seemed to have made a complete recovery from the operation at Montreux, but in the late autumn disturbing symptoms of arterio-sclerosis, brought about by the kidney disease left as a consequence of his early illness, showed themselves and increased in gravity through the early months of the present year. He sank very rapidly at the end and died on April 9th, 1921, at the age of thirty-six.

Although Vernon had been at Cambridge for comparatively so short a time, he had gained the affectionate regard of many of the senior members of the University as well as of the younger men, for his personality was one of singular charm and attractiveness that rapidly won the friendship of all with whom he was more closely associated. His education had been so different from that of the men whom he met in the laboratories and colleges as to give him a fresh and often unconventional outlook on the questions that arose, and the engaging frankness with which he would state his views made him always an interesting companion.

As a chemist he was gifted with quite exceptional experimental skill. All who were familiar with his methods of work were greatly impressed with his powers and know that through his untimely death an investigator of unusual promise has been lost.

W. H. M.

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FORMULA INDEX.

The following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

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CCl_4 Carbon tetrachloride, purification and condensations of (Ingold and Thorpe), 1227.

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CH_2I_2 Methylene iodide, preparation of (Perkin and Scarborough), 1408.

CH_2S_3 Trithiocarbonic acid, salts of (Yeoman), 38.

CH_2S_4 Perthiocarbonic acid, salts of (Yeoman), 38.

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CHO_6N_3 Nitroform, preparation of halogen derivatives of (Macbeth and Pratt), 354; colorations produced by substituted derivatives of (Graham and Macbeth), 1362.

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CO_2NCl_3 Chloropicrin, preparation of (Orton and McKie), 29.

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C_2H_4 Ethylene, propagation of flame in mixtures of air and (Chapman), 1677; action of sulphur monochloride with (Mann, Pope, and Vernon), 634.

2 II

$C_2H_4O_2$ Acetic acid, equilibrium of aniline with (O'Connor), 400; additive compounds of, with benzene and 4′-dimethylamino-2-hydroxydistyryl ketone (Heilbron and Buck), 1511.

C_2H_5I Ethyl iodide, velocity of reaction of sodium β-naphthoxide and (Cox), 149.

C_2H_6O Ethyl alcohol, additive compound of 4′-dimethylamino-2-hydroxydistyryl ketone with (Heilbron and Buck), 1510.

$C_2H_{11}N$ Diethylamine, action of ethyl nitrate on (Gibson and Macbeth), 441.

2 III

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$C_2H_2O_2Cl_2$ Dichloroacetic acid, preparation of esters of (Crompton and Triffitt), 1874.

$C_2H_2Cl_3As$ β-Chlorovinyldichloroarsine (Green and Price), 451.

C_2H_5ONa Sodium ethoxide, action of carbon tetrachloride with (Ingold and Powell), 1228.

$C_2H_5O_3N$ Ethyl nitrate, preparation of (Hepworth), 254; action of diethylamine on (Gibson and Macbeth), 441.

$C_2H_5Br_3Sn$ Ethylstannic tribromide (Druce), 761.

C_2H_6OS Monothioethylene glycol (Bennett), 422; condensation reactions of (Bennett and Whincop), 1860.

$C_2H_6O_2Sn$ Ethylstannic acid, and its salts (Druce), 758.

$C_2H_6O_4S$ Ethyl hydrogen sulphate, equilibrium of the formation of (Dunnicliff and Butler), 1384; potassium salt, dimorphism of (Hammick and Mullaly), 1802.

$C_2H_6N_2S_2$ Methyl dithiocarbazinate (Losanitch), 764.

$C_2H_6N_4S_3$ Sulphidodithiocarbamide, dihydrochloride of (Naik), 1168.

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$C_2H_8O_2Te$ Dimethyltelluronium dihydroxide, nitrates of (Vernon), 694.

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$C_2H_5O_3ClS$ Chloroethanesulphonic acid, sodium salt (Bennett), 420.

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C_3H_6 Propylene, action of sulphur monochloride on (Coffey), 94.

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C_3H_5Cl Allyl chloride, preparation of (Coffey and Ward), 1305.

C_3H_6O Acetone, action of ammonia on (Patterson and McMillan), 269.

Allyl alcohol, preparation of (Coffey and Ward), 1303.

$C_3H_6O_2$ Ethyl formate, influence of neutral salts on the hydrolysis of (Manning), 2079.

Methyl acetate, rate of hydrolysis of (Burrows), 1798.

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$C_3H_7O_3Na$ α-Sodium glyceroxide (Fairbourne and Toms), 1035.

C_3H_8IAs Methylethyliodoarsine (Burrows and Turner), 433.

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$C_3H_5O_2N_2Br$ Bromomalonamide (Backes, West, and Whiteley), 364.

$C_3H_7O_3ClS$ Chloropropanesulphonic acid, barium salt (Coffey), 96; (Pope and Smith), 398.

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$C_4H_6O_2$ Allyl formate, preparation of (Coffey and Ward), 1303.

$C_4H_6O_6$ Tartaric acid, decomposition of, by heat (Chattaway and Ray), 34; complex cupric salts of (Packer and Wark), 1348.

$C_4H_8O_2$ Ethyl acetate, additive compound of 4′-dimethylamino-2-hydroxydistyryl ketone with (Heilbron and Buck), 1510.

$C_4H_{10}O$ Ethyl ether, solubility of, in solutions of sodium chloride (Thorne), 262.

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$C_4H_4Cl_3As$ ββ′-Dichlorodivinylchloroarsine (Green and Price), 452.

$C_4H_6OCl_2$ αβ-Dichlorovinyl ethyl ether, preparation of dichloro- and chlorobromo-acetates from (Crompton and Triffitt), 1874.

$C_4H_7ON_3$ *cyclo*Propanonesemicarbazone (Ingold), 329.

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$C_4H_8Cl_2S_3$ ββ′-Dichlorodiethyl trisulphide (Mann, Pope, and Vernon), 639.

$C_4H_{11}OTl$ Thalliumdiethyl hydroxide, salts of (Goddard), 675.

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$C_4H_8O_2N_2S$ *N*-Sulphidobisacetamide (Naik), 1167.

$C_4H_9O_2N_2Br$ Bromomalondimethylamide (Backes, West, and Whiteley), 365.

$C_4H_9O_3ClS$ β-Chlorobutane-γ-sulphonic acid, barium salt (Pope and Smith), 399.

$C_4H_{12}OI_2Te_2$ Di-iodotetramethylditelluronium oxide (Vernon), 691.

4 V

$C_4H_{17}ON_4Cl_2Co$ *trans*-Dichlorodiethylenediaminecobaltic hydroxide, salts of (Duff), 1987.

C_5 Group.

$C_5H_4O_4$ Δ^2-*cyclo*Propene-1:2-dicarboxylic acid (Farmer and Ingold), 2015.

C_5H_5N Pyridine, additive compound of 4′-dimethylamino-2-methoxydistyryl ketone phenylhydrazone with (Heilbron and Buck), 1520.

$C_5H_6O_5$ *cyclo*Propanol-1:2-dicarboxylic acid, and its silver salt (Ingold), 326.

$C_5H_6O_5$ Lactonic acids of αα′-dihydroxyglutaric acids, and their silver salts (Ingold), 322.

$C_5H_8O_5$ α-Hydroxyglutaric acid (Ingold), 318.

$C_5H_8O_6$ αα′-Dihydroxyglutaric acids (Ingold), 322.

$C_5H_{11}N$ Piperidine, action of, on alkyl nitrates (Gibson and Macbeth), 438; action of, on silicon organic compounds (Kipping and Sands), 848.

5 III

$C_5H_5O_4Br$ 1-Bromo*cyclo*propane-1:2-dicarboxylic acid, and its salts (Ingold), 325.

$C_5H_6O_3N_2$ 4-Nitro-3:5-dimethyl*iso*oxazole (Morgan and Burgess), 699.

$C_5H_6O_4Br_2$ Dibromoglutaric acids (Ingold), 317.

$C_5H_7O_2N$ Ethyl cyanoacetate, syntheses by means of (Ingold), 329, 341; (Ingold and Perren), 1582, 1865; sodium derivative, condensation of carbon tetrachloride with (Ingold and Powell), 1229.

$C_5H_7O_2N_3$ 3:5-Dimethyl*iso*oxazole-4-diazonium hydroxide, salts of (MORGAN and BURGESS), 702.

$C_5H_8ON_2$ 4-Amino-3:5-dimethyl*iso*oxazole, and its hydrochloride (MORGAN and BURGESS), 700.

$C_5H_{15}O_2N$ Choline, crystalline, preparation of (DUDLEY), 1260.

5 IV

$C_5H_2ON_6Fe$ Nitroprussic acid, and its salts (BURROWS and TURNER), 1450.

C_5H_6ONI 4-Iodo-3:5-dimethyl*iso*oxazole (MORGAN and BURGESS), 1547.

$C_5H_8O_2Br_2Te$ Tellurium acetylacetone dibromide (MORGAN and DREW), 616.

$C_5H_8O_2I_2Te$ Tellurium acetylacetone di-iodide (MORGAN and DREW), 617.

$C_5H_8O_2N_2S_2$ Dithiomesoxodimethylamide (NAIK), 384.

C_6 Group.

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C_6H_{12} β-Ethyl-Δ^{α}-butylene (KON), 821.

6 II

$C_6H_4O_2$ *p*-Benzoquinone, additive compound of 4′-dimethylamino-2-hydroxydistyryl ketone with (HEILBRON and BUCK), 1511.

C_6H_6O Phenol, additive compound of 4′-dimethylamino-2-hydroxydistyryl ketone with (HEILBRON and BUCK), 1511.

C_6H_7N Aniline, equilibrium of acetic acid with (O'CONNOR), 400; velocity of reaction of ω-bromoacetophenone and (COX), 145.

$C_6H_8O_5$ Methoxy*cyclo*propane-1:2-dicarboxylic acid, and its silver salt (INGOLD), 327.

$C_6H_{10}O_5$ β-Glucosan, preparation and relationships of (IRVINE and OLDHAM), 1744.

α-Methoxyglutaric acid, and its silver salt (INGOLD), 320.

$C_6H_{11}N_3$ 4-β-Methylaminoethylglyoxaline, and its salts (FARGHER and PYMAN), 734.

$C_6H_{12}O_6$ Dextrose, mutarotation of, and its catalysis by metals (GARNER and JACKMAN), 1936.

$C_6H_{12}N_4$ Hexamethylenetetramine, compounds of, with metallic salts and acids (RÂY and SARKAR), 390.

6 III

$C_6H_3O_6N_3$ *s*-Trinitrobenzene, additive compounds of, with 4′-dimethylamino-2-hydroxydistyryl ketone and 4′-dimethylamino-2-methoxydistyryl ketone (HEILBRON and BUCK), 1511.

$C_6H_3O_7N_3$ Picric acid, preparation of (KING), 2105; equilibrium of 5-phenylacridine with (BASSETT and SIMMONS), 416.

$C_6H_3O_{12}Fe$ Ferrioxalic acid, potassium salt (THOMAS), 1140.

$C_6H_4O_4N_2$ *m*-Dinitrobenzene, additive compounds of, with 4′-dimethylamino-2-hydroxydistyryl ketone and 4′-dimethylamino-2-methoxydistyryl ketone (HEILBRON and BUCK), 1511.

$C_6H_4O_5N_2$ Dinitrophenols, influence of position on the solubility and volatility of (SIDGWICK and ALDOUS), 1001.

$C_6H_5O_3N$ Nitrophenols, influence of position on the solubility and volatility of (SIDGWICK and ALDOUS), 1001.

$C_6H_5Br_2Bi$ Phenyldibromobismuthine, preparation of (CHALLENGER and ALLPRESS), 919.

$C_6H_6O_2N_2$ Nitroanilines, solubility and volatility of (SIDGWICK and RUBIE), 1013.

C_6H_6NCl Chloroanilines, solubility and volatility of (Sidgwick and Rubie), 1013.

$C_6H_6Cl_3As$ ββ′β″-Trichlorotrivinylarsine (Green and Price), 452.

C_6H_7ON δ-Benzildioxime (Atack and Whinyates), 1184.

β-Phenylhydroxylamine, preparation of, from nitrobenzene (Lapworth and Pearson), 765.

$C_6H_8O_4Br_2$ Dibromoadipic acids (Perkin and Robinson), 1392.

$C_6H_8O_4I_2$ Di-iodoadipic acids (Ingold), 964.

C_6H_8NI Methylpyridinium iodide, mercuri-iodide of, and its crystallography (Porter), 1770.

$C_6H_{12}N_2S_4$ Methyl bismethyldithiocarbamate (Losanitch), 765.

$C_6H_{12}Cl_2S$ ββ′-Dichlorodi-*n*-propyl sulphide (Coffey), 97; (Pope and Smith), 397.

$C_6H_{12}Cl_2S_2$ Ethylene bis-β-chloroethyl sulphide (Bennett and Whincop), 1862.

$C_6H_{14}O_2S$ ββ′-Dihydroxydi-*n*-propyl sulphide (Coffey), 96.

$C_6H_{14}O_2S_2$ Ethylene bis-β-hydroxyethyl sulphide (Bennett and Whincop), 1862.

6 IV

C_6H_4ONCl *o*- and *m*-Chloronitrosobenzenes (Haworth and Lapworth), 772.

$C_6H_5O_6NS$ 6-Nitrophenol-*o*-sulphonic acid, and its salts (King), 1417.

C_6H_6ONCl *m*-Chlorophenylhydroxylamine (Haworth and Lapworth), 773.

$C_6H_6O_2N_3Cl$ 2-Chloro-5-nitrophenylhydrazine (Perkin and Plant), 1837.

$C_6H_6O_6N_2S$ Nitroaminophenol-*o*-sulphonic acids (King), 1418.

$C_6H_7O_4NS$ 6-Aminophenol-*o*-sulphonic acid (King), 1117, 1417.

$C_6H_8O_4N_2S$ 4:6-Diaminophenol-*o*-sulphonic acid (King), 1419.

$C_6H_{18}O_2I_2Te_3$ Di-iodohexamethyltritelluronium dioxide (Vernon), 690.

6 V

$C_6H_8O_6NSAs$ 3-Amino-4-hydroxy-5-sulphinophenylarsinic acid (King), 1113.

3-Amino-4-hydroxy-5-sulphophenylarsenious acid (King), 1420.

$C_6H_8O_7NSAs$ 3-Amino-4-hydroxy-5-sulphophenylarsinic acid (King), 1114.

C_7 Group.

C_7H_8 Toluene, sulphonation of, with chlorosulphonic acid (Harding), 1261.

7 II

C_7H_6O Benzaldehyde, condensation of *m*-dimethylaminophenol with (Krishna and Pope), 286.

$C_7H_6O_2$ Salicylaldehyde, additive compounds of 4′-dimethylamino-2-hydroxydistyryl ketone with (Heilbron and Buck), 1512.

$C_7H_6O_5$ Gallic acid, condensation of chloral with (Alimchandani and Meldrum), 201.

$C_7H_6Cl_2$ *m*-Chlorobenzyl chloride (Kenner and Witham), 1460.

$C_7H_8O_2$ Dimethylpyrone, action of iodine and barium hydroxide on (Collie and Reilly), 1550.

$C_7H_8O_5$ Anhydro-acid from methanetriacetic acid (Ingold), 353.

$C_7H_8N_2$ 1:1-Dimethyl*cyclo*propane-2:3-dicarboxylonitrile (Birch, Gough, and Kon), 1322.

$C_7H_{10}O_4$ *cis*- and *trans*-1:1-Dimethyl*cyclo*propane-2:3-dicarboxylic acids (Birch, Gough, and Kon), 1322.

$C_7H_{10}O_6$ Methanetriacetic acid, preparation of (Ingold), 352.

$C_7H_{12}O_4$ Diethyl malonate, sodium derivative, condensations of αβ-unsaturated esters with (Ingold and Powell), 1976.

7 III

$C_7H_5O_3N_3$ Nitro-3-keto-1:3-dihydroindazoles, and their sodium salts (Kenner and Witham), 1055.

$C_7H_5O_4N_5$ 2:4-Dinitro-*m*-tolylazoimide (Brady and Bowman), 898.

$C_7H_5O_6N_3$ 2:4:6-Trinitrotoluene, additive compound of 4′-dimethylamino-2-hydroxydistyryl ketone with (Heilbron and Buck), 1511.

$C_7H_5O_8N_5$ Trinitrophenylmethylnitroamine (*tetryl*), thermal decomposition of (Hinshelwood), 722.

$C_7H_5O_9N_5$ Trinitrohydroxyphenylmethylnitroamine, thermal decomposition of (Hinshelwood), 722.

$C_7H_6O_3N_4$ 4-Nitro-1-hydroxymethyl-1:2:3-benzotriazoles (Brady and Bowman), 898.

$C_7H_6O_4N_2$ 2:4-Dinitrotoluene, additive compound of 4′-dimethylamino-2-hydroxydistyryl ketone with (Heilbron and Buck), 1511.

Dinitrotoluenes, partial reduction of (Burton and Kenner), 1047.

$C_7H_7ON_3$ 5-Amino-3-keto-1:3-dihydroindazole, and its hydrochloride (Kenner and Witham), 1056.

$C_7H_7O_2N_3$ Nitroformaldehydephenylhydrazone, tautomerism of (Sidgwick and Ewbank), 491.

$C_7H_7O_3I$ Substance and its salts, from dimethylpyrone, barium hydroxide, and iodine (Collie and Reilly), 1553.

$C_7H_7NS_2$ Phenyldithiocarbamic acid, hydrazine salt (Losanitch), 765.

$C_7H_7Cl_2Bi$ *p*-Tolyldichlorobismuthine (Challenger and Allpress), 917.

$C_7H_8O_2N_2$ 2-Nitro-*m*-toluidine (Burton and Kenner), 1052.

$C_7H_8O_4N_4$ Dinitrotolylhydrazines (Brady and Bowman), 894.

$C_7H_8O_4Br_2$ *cis*-1:3-Dibromo*cyclo*pentane-1:3-dicarboxylic acid (Perkin and Scarborough), 1407.

$C_7H_8N_2S_2$ Phenyldithiocarbazinic acid, hydrazine salt (Losanitch), 765.

$C_7H_9O_2N$ Caronimide (Birch, Gough, and Kon), 1322.

$C_7H_9N_2Cl$ 2-Chloro-3:4-tolylenediamine (Morgan and Glover), 1706.

$C_7H_{10}ON_2$ *m*-Methoxyphenylhydrazine (Kermack, Perkin, and Robinson), 1640.

$C_7H_{10}O_2N_2$ 4-Acetylamino-3:5-dimethyl*iso*oxazole (Morgan and Burgess), 701.

$C_7H_{10}O_4Br_2$ Methyl αα′-dibromoglutarate (Ingold), 317.

$C_7H_{10}NI$ Ethylpyridinium iodide, mercuri-iodide of, and its crystallography (Porter), 1770.

Methyl-α-picolinium iodide, mercuri-iodide of, and its crystallography (Porter), 1772.

$C_7H_{11}O_2N_3$ *dl*-α-Methylamino-β-glyoxaline-4-propionic acid, and its salts (Fargher and Pyman), 736.

$C_7H_{11}O_3N$ Ethyl α-carbamylcrotonate (Gupta), 303.

$C_7H_{18}O_3N_2$ Glycylcholine, and its salts (Dudley), 1256.

7 IV

$C_7H_4O_2N_3Cl$ 3-Chloro-5-nitroindazole (Kenner and Witham), 1057.

$C_7H_4O_4NCl$ *o*-Chlorodinitrotoluenes (Morgan and Jones), 187.

$C_7H_5O_2Cl_2S$ 2:6-Dichloro-*p*-toluenesulphonyl chloride (Davies), 872.

$C_7H_5O_4N_2Cl$ 3-Chloro-2:4-dinitrotoluene (Brady and Bowman), 897.

o-Chlorodinitrotoluenes (Morgan and Challenor), 1537; (Morgan and Glover), 1700.

$C_7H_5O_4N_2I$ 3-Iodo-2:4-dinitrotoluene (Brady and Bowman), 897.

$C_7H_6ON_3Cl$ 4-Chloro-1-hydroxy-5-methyl-1:2:3-benzotriazole, and its hydrazine salt (Morgan and Glover), 1705.

$C_7H_6O_2NCl$ *p*-Nitrobenzyl chloride, condensation of nitroso-compounds with (Barrow and Griffiths), 212.

$C_7H_6O_2Cl_2S$ 2-Chloro-*p*-toluenesulphonyl chloride, preparation and nitration of (Davies), 860.

6-Chloro-*o*-toluenesulphonyl chloride (Davies), 878.

$C_7H_6O_3NCl$ 2-Chloro-5-nitro-*p*-cresol, and its salts (Davies), 866.

$C_7H_6O_3Cl_2S$ 2:6-Dichloro-*p*-toluenesulphonic acid, and its salts (Davies), 872.

$C_7H_6O_4N_3Cl$ 2-Chloro-3:5-dinitro-*p*-toluidine (Davies), 868.

$C_7H_6NClBr_2$ 6-Chloro-2:4-dibromo-*m*-toluidine (Davies), 866.

$C_7H_7O_2N_2Cl$ 2- and 6-Chloro-4-nitro-*m*-toluidines (Morgan, Challenor, and Jones), 1544; (Morgan and Glover), 1704.

$C_7H_7O_2ClS$ *o*- and *p*-Toluenesulphonyl chlorides, melting points of mixtures of (Harding), 260.

$C_7H_7O_3ClS$ 6-Chloro-*o*-toluenesulphonic acid, and its salts (Davies), 879.

$C_7H_{11}O_2Cl_3Te$ Tellurium O-ethylacetylacetone trichloride (Morgan and Drew), 613.

$C_7H_{12}O_2N_2Br_2$ Dibromomalondiethylamide (Backes, West, and Whiteley), 367.

$C_7H_{13}O_2N_2Br$ Bromomalondiethylamide (Backes, West, and Whiteley), 366.

7 V

$C_7H_4O_3NClS$ 6-Chloro-*o*-benzoicsulphinide (Davies), 880.

$C_7H_5O_4NCl_2S$ Chloronitro-*o*- and -*p*-toluenesulphonyl chlorides (Davies), 864, 870, 884.

$C_7H_6O_5NClS$ Chloronitro-*o*- and -*p*-toluenesulphonic acids, and their salts (Davies), 865, 870, 884.

$C_7H_7O_2NCl_2S$ 2:6-Dichloro-*p*-toluenesulphonamide (Davies), 872.

$C_7H_7O_4N_2ClS$ Chloronitro-*o*- and -*p*-toluenesulphonamides (Davies), 865, 870, 884.

$C_7H_8O_2NClS$ 6-Chloro-*o*-toluenesulphonamide (Davies), 879.

$C_7H_8O_3NClS$ 6-Chloro-*m*-toluidine-4-sulphonic acid (Davies), 865.

C_8 Group.

C_8H_{16} 1:1-Dimethyl*cyclo*hexane from methylheptenone (Crossley and Renouf), 271.

8 II

$C_8H_6O_6$ Carboxymethanetriacetic dianhydride (Ingold and Powell), 1873.

$C_8H_8O_2$ Anisaldehyde, additive compound of 4′-dimethylamino-2-hydroxydistyryl ketone with (Heilbron and Buck), 1512.

Phenyl acetate, action of sodium on (Perkin), 1284.

$C_8H_8O_3$ Cresotic acids, condensation of chloral with (Alimchandani and Meldrum), 201.

$C_8H_9N_3$ 6-Amino-5-methylindazole (Pearman), 718.

$C_8H_{10}O_6$ Lactone of β-hydroxy-β-methylbutane-γδδ-tricarboxylic acid (Birch, Gough, and Kon), 1323.

cis- and *trans*-*cyclo*Pentane-1:2:3-tricarboxylic acids, synthesis and resolution of (Perkin and Robinson), 1392.

$C_8H_{10}O_8$ *n*-Butane-αβγδ-tetracarboxylic acid (Ingold), 348.

$C_8H_{10}O_8$ Carboxymethanetriacetic acid, and its salts (Ingold and Powell), 1869.

$C_8H_{11}As$ Phenyldimethylarsine, additive compounds of, with arsenic and phosphorus iodides, and metallic iodides (Burrows and Turner), 1449.

$C_8H_{12}O$ *cyclo*Pentenylacetone (Kon), 823.

$C_8H_{12}O_3$ Ethyl *cyclo*pentanone-3-carboxylate (Ingold and Thorpe), 500.

$C_8H_{12}O_4$ *cyclo*Pentane-1-acetic-1-carboxylic acid (Norris and Thorpe), 1208.

$C_8H_{12}O_6$ ω-Methylmethanetriacetic acid (Ingold and Perren), 1599, 1868.

$C_8H_{14}O$ Ketone, from ββ-diethylglutaric acid (Kon), 821.

*cyclo*Pentylacetone (Kon), 824.

$C_8H_{16}O$ Ketone, from reduction of ketone $C_8H_{14}O$ (Kon), 822.

$C_8H_{16}S_2$ Tetramethyldiethylene disulphide (Pope and Smith), 400.

8 III

$C_8H_4O_4N_2$ 6-Nitro-3:4-methylenedioxybenzonitrile (Keffler), 1478.

$C_8H_5O_4Cl$ 4-Chlorophthalic acid, preparation of (Moore, Marrack, and Proud), 1788.

$C_8H_5NCl_2$ 3-Chloro-2-cyanobenzyl chloride (Kenner and Witham), 1458.

C_8H_6OS 3-Oxy(1)thionaphthen, preparation and derivatives of (Smiles and McClelland), 1810.

$C_8H_6O_3N$ Hydantoin from 6-carbamido-*m*-hydroxybenzoic acid (Froelicher and Cohen), 1432.

C_8H_6NCl 3-Chloro-*o*-toluonitrile (Kenner and Witham), 1458.

C_8H_7OBr ω-Bromoacetophenone, velocity of reaction of aniline and (Cox), 145.

$C_8H_7O_2Cl$ 3-Chloro-*o*-toluic acid (Kenner and Witham), 1458.

$C_8H_7O_7N_5$ 2:4:6-Trinitrotolylmethylnitrosoamine (Brady and Gibson), 104.

$C_8H_7O_8N_5$ 2:4:6-Trinitrotolylmethylnitroamine (Brady and Gibson), 98.

$C_8H_7N_2Cl$ 5-Chloro-6-methylbenziminazole (Morgan and Challenor), 1542.

$C_8H_8O_2N_2$ 2:3-Dicyano-1:1-dimethyl*cyclo*propane-2-carboxylic acid (Birch, Gough, and Kon), 1320.

$C_8H_8O_2S$ *m*-Methylthiolbenzoic acid (Smiles and Stewart), 1797.

$C_8H_8O_3N_2$ *o*-Carbamidobenzoic acid, preparation of (Scott and Cohen), 664.

Nitroacetanilides, solubility and volatility of (Sidgwick and Rubie), 1013.

$C_8H_8O_4N_2$ Carbamido-*m*-hydroxybenzoic acids (Froelicher and Cohen), 1430.

$C_8H_8O_4N_4$ Formaldehyde-2:4-dinitro-*m*-tolylhydrazone (Brady and Bowman), 899.

$C_8H_8O_4S$ *m*-Methylsulphonebenzoic acid (Smiles and Stewart), 1797.

$C_8H_8O_5N_4$ Dinitrotolylmethylnitrosoamines (Brady and Gibson), 103.

$C_8H_8O_6N_2$ 2:4-Dinitrophenyl-β-hydroxyethyl ether (Fairbourne and Toms), 2077.

$C_8H_8O_6N_4$ Dinitrotolylmethylnitroamines (Brady and Gibson), 103.

$C_8H_8N_3Cl$ 6-Chloro-2-methyl-2:3-tolylenediazoimine (Morgan and Jones), 191.

$C_8H_9ON_3$ 2:3-Dicyano-1:1-dimethyl*cyclo*propane-2-carboxylamide (Birch, Gough, and Kon), 1320.

$C_8H_9O_3N$ Amino-*m*-methoxybenzoic acids (Froelicher and Cohen), 1430.

$C_8H_9O_3N_3$ Acetyl-*p*-nitrophenylhydrazine (Morgan and Drew), 622.

$C_8H_9O_4N_3$ Dinitromethyltoluidines (Brady and Gibson), 101.

$C_8H_{10}ON_2$ 6-Amino-2:3-dihydro-1:4-benz*iso*oxazine (FAIRBOURNE and TOMS), 2078.

$C_8H_{10}O_2N_2$ *p*-Aminophenylaminoacetic acid, hydrochlorides of (GRANT and PYMAN), 1901.

$C_8H_{11}ON$ *m*-Dimethylaminophenol, condensation of benzaldehyde with (KRISHNA and POPE), 286.

$C_8H_{11}O_5N_3$ *cyclo*Pentanone-3:4-dicarboxylic acid semicarbazone (INGOLD), 350.

$C_8H_{11}N_2Cl$ 6-Chloro-2-methyl-2:3-tolylenediamine (MORGAN and JONES), 191.

6-Chloro-3-N-methyl-3:4-tolylenediamine (MORGAN and CHALLENOR), 1542.

$C_8H_{12}NI$ Ethyl-*a*-picolinium iodide, mercuri-iodide of, and its crystallography (PORTER), 1772.

Propylpyridinium iodide, mercuri-iodide of, and its crystallography (PORTER), 1771.

$C_8H_{13}O_2N$ Ethyl cyanomethylbutyrates (INGOLD), 339.

$C_8H_{15}ON$ Oxime of ketone $C_8H_{14}O$ (KON), 822.

$C_8H_{16}Cl_2S$ $\beta\beta'$-Dichlorodi-*sec.*-butyl sulphide (POPE and SMITH), 399.

$C_8H_{17}ON$ 1-Ethoxymethylpiperidine, preparation of (MCLEOD and ROBINSON), 1474.

8 IV

$C_8H_5O_2N_2Cl$ Substance, from sodium hypochlorite and 2:4-diketo-1:2:3:4-tetrahydroquinazoline (SCOTT and COHEN), 665.

$C_8H_6O_4NCl$ Methyl 2-chloro-3-nitrobenzoate (KENNER and STUBBINGS), 598.

C_8H_8ONCl Chloroacetanilides, solubility and volatility of (SIDGWICK and RUBIE), 1013.

3-Chloro-*o*-toluamide (KENNER and WITHAM), 1458.

$C_8H_8O_3N_3Cl$ Chloronitrotolylmethylnitrosoamines (MORGAN and JONES), 189.

$C_8H_8O_5N_2S$ 2:4-Dinitrophenyl β-hydroxyethyl sulphide (BENNETT and WHINCOP), 1864.

$C_8H_9O_2N_2Cl$ Chloronitro-N-methyltoluidines (MORGAN and JONES), 189.

$C_8H_{10}O_2ClBr$ 4-Chloro-4-bromo-1:1-dimethyl*cyclo*hexane-3:5-dione (NORRIS and THORPE), 1210.

$C_8H_{10}O_3NTl$ Thalliumdimethyl nitrophenoxides (GODDARD), 1312.

$C_8H_{10}O_5N_3Tl$ Thalliumdimethyl 4:6-dinitro-2-aminophenoxide (GODDARD), 1313.

$C_8H_{16}O_2N_2S$ N-Sulphidobisbutyramide (NAIK), 1168.

$C_8H_{16}O_2Cl_2S$ $\beta\beta'$-Dichloro-di-*sec.*-butylsulphone (POPE and SMITH), 399.

$C_8H_{18}O_2S_3$ Sulphidobis-β-hydroxydiethyl sulphide (BENNETT and WHINCOP), 1863.

$C_8H_{19}O_5N_4Co$ *cis*-Maleatodiethylenediaminecobaltic hydroxide, salts of (DUFF), 388.

$C_8H_{21}O_5N_4Co$ *cis*-Succinatodiethylenediaminecobaltic hydroxide, salts of (DUFF), 387.

$C_8H_{21}O_7N_4Co$ *cis*-Mesotartratodiethylenediaminecobaltic hydroxide, salts of (DUFF), 388.

8 V

$C_8H_7O_4N_2ClS$ 2:4-Dinitrophenyl β-chloroethyl sulphide (BENNETT and WHINCOP), 1864.

$C_8H_7O_4N_2BrS$ 2:4-Dinitrophenyl β-bromoethyl sulphide (BENNETT and WHINCOP), 1864.

$C_8H_7O_5N_2ClS$ 2:4-Dinitrophenyl β-chloroethyl sulphoxide (BENNETT and WHINCOP), 1864.

$C_8H_7O_5N_2BrS$ 2:4-Dinitrophenyl β-bromoethyl sulphoxide (BENNETT and WHINCOP), 1864.

$C_8H_{18}O_4N_4BrCo$ *cis*-Maleatodiethylenediaminecobaltic bromide (+ $2H_2O$) (DUFF), 388.

$C_8H_{18}O_4N_4Br_3Co$ *cis*-Dibromosuccinatodiethylenediaminecobaltic bromide (+ $2H_2O$) (DUFF), 389.

$C_8H_{19}O_5N_4Br_2Co$ *cis*-Dibromosuccinatodiethylenediaminecobaltic hydroxide (DUFF), 389.

$C_8H_{20}O_4N_4BrCo$ *cis*-Succinatodiethylenediaminecobaltic bromide (+ $2H_2O$) (DUFF), 387.

$C_8H_{20}O_6N_4BrCo$ *cis*-Mesotartratodiethylenediaminecobaltic bromide (+ $2H_2O$) (DUFF), 388.

C_9 Group.

$C_9H_8N_2$ 4-Phenylglyoxaline, and its salts (GRANT and PYMAN), 1896.

$C_9H_{10}O_3$ Atrolactinic acid, resolution of (WREN and WRIGHT), 798.

α-Hydroxy-β-phenylpropionic acid (WREN and WRIGHT), 798.

$C_9H_{10}O_4$ Phenylglyceric acid, action of fused potassium hydroxide on (LE SUEUR and WOOD), 1697.

$C_9H_{10}N_4$ 5-Amino-4-*p*-aminophenylglyoxaline, dihydrochloride of (GRANT and PYMAN), 1900.

$C_9H_{12}O_3$ *cyclo*Hexane-1-acetic-1-carboxylic anhydride (NORRIS and THORPE), 1206.

$C_9H_{12}O_8$ Acid, from oxidation of *cyclo*hexane-1:1-diacetic acid (INGOLD and POWELL), 1870.

$C_9H_{14}O_4$ *cyclo*Hexane-1-acetic-1-carboxylic acid, and its silver salt (NORRIS and THORPE), 1206.

$C_9H_{14}O_7$ Trimethyl saccharolactonic acid (IRVINE and OLDHAM), 1757.

$C_9H_{16}O_5$ Ethyl α-hydroxyglutarate (INGOLD), 318.

Trimethyl β-glucosan, preparation of (IRVINE and OLDHAM), 1754.

9 III

$C_9H_5O_5Cl_3$ 3:4:5-Trihydroxy-2-trichloromethylphthalide (ALIMCHANDANI and MELDRUM), 206.

$C_9H_6O_4N_2$ Diketotetrahydroquinazolinecarboxylic acid, and its sodium salt (SCOTT and COHEN), 667.

$C_9H_6O_4N_4$ 5-Nitro-4-*p*-nitrophenylglyoxaline, and its nitrate (GRANT and PYMAN), 1898.

C_9H_7OCl Chloro-1-hydrindones (KENNER and WITHAM), 1459.

$C_9H_7O_2N_3$ 4-Nitrophenylglyoxalines, and their salts (GRANT and PYMAN), 1897.

$C_9H_7O_3N_3$ 5-Nitro-4-*p*-hydroxyphenylglyoxaline (GRANT and PYMAN), 1902.

$C_9H_7O_4N_3$ Acetyl derivative of 5-nitro-3-keto-1:3-dihydroindazole (KENNER and WITHAM), 1055.

$C_9H_8O_2N_4$ 5-Nitro-4-*p*-aminophenylglyoxaline, and its dihydrochloride (GRANT and PYMAN), 1901.

$C_9H_8O_4N_2$ 6-Nitroveratronitrile (KEFFLER), 1479.

$C_9H_8O_5N_2$ 3-Carbamidophthalic acid (+ $\frac{1}{2}H_2O$) (SCOTT and COHEN), 666.

$C_9H_8N_2S$ 2-Thiol-4-phenylglyoxaline, and its salts (GRANT and PYMAN), 1895.

C_9H_9ON 6-Methoxyindole (KERMACK, PERKIN, and ROBINSON), 1632.

$C_9H_9O_2Cl$ 5-Chloro-2:4-dimethylbenzoic acid (Morgan and Hickinbottom), 1891.
β-*m*-Chlorophenylpropionic acid (Kenner and Witham), 1460.
$C_9H_9O_2Br$ 5-Bromo-2-methoxyphenylacetaldehyde (Read and Andrews), 1785.
$C_9H_9O_3Cl$ Cinnamic acid chlorohydrin, preparation of (Read and Andrews), 1777.
$C_9H_9O_3Br$ Cinnamic acid bromohydrin, and its salts (Read and Andrews), 1778.
$C_9H_9O_4I$ Acetyl derivative of substance $C_7H_7O_3I$ (Collie and Reilly), 1554.
$C_9H_9O_5N$ *o*-Nitro-*p*-methoxyphenylacetic acid (Kermack, Perkin, and Robinson), 1631.
3-Nitro-2-methoxy-*p*-toluic acid (Simonsen and Rau), 1342.
$C_9H_9O_5N_3$ 4:5-Dinitroaceto-*o*-toluidide (Morgan and Glover), 1703.
$C_9H_9O_{12}Co$ Cobaltimalonic acid, potassium salt (Thomas), 1140.
$C_9H_9N_2Cl$ 5-Chloro-1:6-dimethylbenziminazole (Morgan and Challenor), 1541.
$C_9H_{10}O_2N_2$ Malonphenylamide (+ $\frac{1}{2}H_2O$) (Backes, West, and Whiteley), 372.
$C_9H_{10}O_3N_2$ 2-Nitroaceto-*m*-toluidide (Burton and Kenner), 1052.
$C_9H_{10}O_4N_2$ Carbamido-*m*-methoxybenzoic acids (Froelicher and Cohen), 1430.
3-Nitro-2-methoxy-*p*-toluamide (Simonsen and Rau), 1342.
$C_9H_{10}O_4N_4$ Acetaldehyde-2:4-dinitro-*m*-tolylhydrazone (Brady and Bowman), 899.
$C_9H_{10}O_5N_2$ αβ-Dicyano-γ-hydroxy-γ-methylbutane-αβ-dicarboxylic acid, and its silver salt (Birch, Gough, and Kon), 1323.
$C_9H_{10}O_5N_4$ Acetyl-2:4-dinitro-*m*-tolylhydrazine (Brady and Bowman), 897.
$C_9H_{11}ON$ *p*-Dimethylaminobenzaldehyde, additive compound of, with 4′-dimethylamino-2-hydroxydistyryl ketone (Heilbron and Buck), 1507.
$C_9H_{11}O_2N_3$ *p*-Acetylaminonitrosomethylaniline (Perkin and Plant), 1835.
$C_9H_{11}O_3N$ 3-Amino-2-methoxy-*p*-toluic acid, and its salts (Simonsen and Rau), 1343.
β-Hydroxy-β-3:4-methylenedioxyphenylethylamine, and its salts (Mason), 1077.
$C_9H_{11}O_4N_3$ Dinitrodimethyltoluidines (Brady and Gibson), 102.
4-Nitro-2-carbethoxyphenylhydrazine (Kenner and Witham), 1055.
$C_9H_{12}O_4Br_2$ Methyl *cis*-1:3-dibromo*cyclo*pentane-1:3-dicarboxylate (Perkin and Scarborough), 1407.
$C_9H_{13}ON_3$ *p*-Acetylaminophenylmethylhydrazine (Perkin and Plant), 1835.
$C_9H_{13}O_4Br$ Ethyl α-bromoglutaconate (Farmer and Ingold), 2013.
$C_9H_{14}O_4Br_2$ Ethyl αα′-dibromoglutarate (Ingold), 318.
$C_9H_{14}NI$ Propyl-α-picolinium iodide, mercuri-iodide of, and its crystallography (Porter), 1773.
$C_9H_{15}ON_3$ Semicarbazone of *cyclo*pentenylacetone (Kon), 823.
$C_9H_{15}OAs$ Phenyltrimethylarsonium hydroxide, cadmi-iodide of (Burrows and Turner), 1449.
$C_9H_{15}O_4Br$ Ethyl α-bromoglutarate (Ingold), 316.
$C_9H_{15}N_2I$ Phenylmethylethylazonium iodide, additive compound of thiocarbamide and (Singh and Lal), 211.
$C_9H_{17}ON_3$ Semicarbazone of ketone $C_8H_{14}O$ (Kon), 821.
Semicarbazone of *cyclo*pentylacetone (Kon), 824.

$C_9H_{18}O_2N_2$ Malondi-*n*-propylamide (Backes, West, and Whiteley), 367.

$C_9H_{19}ON_3$ Semicarbazone of ketone $C_8H_{16}O$ (Kon), 822.

9 IV

$C_9H_6O_2NCl$ 5-Chloro*iso*nitroso-1-hydrindone (Kenner and Witham), 1461.

$C_9H_6O_2N_2Br_4$ Dibromomalondibromophenylamide (Backes, West, and Whiteley), 373.

$C_9H_7O_2N_2Br_3$ Dibromomalonbromophenylamide (Backes, West, and Whiteley), 373.

C_9H_8ONCl Oxime of 5-chloro-1-hydrindone (Kenner and Witham), 1461.

$C_9H_8O_2N_2Br_2$ Bromomalonbromophenylamide (Backes, West, and Whiteley), 373.

Malondibromophenylamide (Backes, West, and Whiteley), 373.

$C_9H_8O_2N_2S_2$ Dithiomesoxomonophenylamide (Naik), 1237.

$C_9H_8O_4NCl$ Ethyl 2-chloro-3-nitrobenzoate (Kenner and Stubbings), 598.

Ethyl chloronitrobenzoates, condensation of, with hydrazines (Kenner and Witham), 1053.

$C_9H_8O_4NI$ Ethyl 2-iodo-3-nitrobenzoate (Kenner and Stubbings), 599.

$C_9H_8O_5N_2Br_2$ 2:4-Dinitrophenyl $\beta\gamma$-dibromopropyl ether (Fairbourne and Toms), 1038.

$C_9H_8O_5N_3Cl$ 2-Chloro-3:5-dinitroaceto-*p*-toluidide (Davies), 868.

$C_9H_9O_2N_2Cl$ Formate of 5-chloro-6-methylbenziminazole (Morgan and Challenor), 1542.

$C_9H_{10}ON_2S$ ω-Aminoacetophenone thiocyanate (Grant and Pyman), 1896.

$C_9H_{11}O_2NS$ β-Hydroxyethyl phenylthiocarbamate (Bennett and Whincop), 1861.

$C_9H_{12}O_3NTl$ Thalliumdimethyl 3-nitro-*o*-tolyloxide (Goddard), 1314.

$C_9H_{13}O_6N_2Br$ Bromomalonyldiurethane (Backes, West, and Whiteley), 372.

$C_9H_{16}O_2N_2Br_2$ Dibromomalondi-*n*-propylamide (Backes, West, and Whiteley), 368.

$C_9H_{17}O_2N_2Br$ Bromomalondi-*n*-propylamide (Backes, West, and Whiteley), 367.

$C_9H_{21}O_5N_4Co$ *cis*Citraconatodiethylenediaminecobaltic hydroxide, hydrogen citraconate of (Duff), 389.

C_{10} Group.

$C_{10}H_{12}$ Tetrahydronaphthalene, preparation of derivatives of (Kon and Stevenson), 87.

$C_{10}H_{16}$ Hydrocarbon, from *Andropogon Jwarancusa* (Simonsen), 1649.

10 II

$C_{10}H_8O_4$ 3-Methoxy-4-methyl-*o*-phthalic anhydride (Simonsen and Rau), 1344.

$C_{10}H_9N$ Quinaldine, synthesis of (Mills, Harris, and Lambourne), 1294.

$C_{10}H_{10}O$ *ar*-Dihydro-α-naphthols (Rowe and Levin), 2021.

$C_{10}H_{10}O_5$ 6-Hydroxy-5-carboxy-*m*-tolylacetic acid, and its silver salt (Alimchandani and Meldrum), 209.

3-Methoxy-4-methyl-*o*-phthalic acid, and its salts (Simonsen and Rau), 1345.

m-Opianic acid, and its silver salt (Fargher and Perkin), 1739.

$C_{10}H_{10}N_2$ 6-Aminoquinaldine (Hamer), 1435.

$C_{10}H_{11}Cl$ 4-Chlorobutenylbenzene (Morgan and Hickinbottom), 1886.

$C_{10}H_{12}O_2$ *n*- and *iso*-Eugenols, analysis of mixtures of (McKie), 777.

Hydroxyphenyl *n*-propyl ketones (Morgan and Hickinbottom), 1884.

$C_{10}H_{12}O_3$ 5-Hydroxy-4-methoxy-*o*-tolyl methyl ketone (Fargher and Perkin), 1733.

$C_{10}H_{12}O_5$ Ethyl 6-ethoxy-2-pyrone-5-carboxylate (Ingold and Perren), 1601.

$C_{10}H_{12}N_2$ *cyclo*Hexane*spirocyclo*propane-2:3-dicarboxylonitrile (Birch, Gough, and Kon), 1325.

1:4-*endo*Methylene-6-methyltetrahydroquinoxaline, and its salts (Moore and Doubleday), 1172.

$C_{10}H_{13}Cl$ 4-Chloro-*n*-butylbenzene (Morgan and Hickinbottom), 1886.

$C_{10}H_{13}As$ *As*-Methyltetrahydroarsinoline, and its salts (Burrows and Turner), 430.

$C_{10}H_{14}O_2$ *cyclo*Pentane*spirocyclo*hexane-3:5-dione (Norris and Thorpe), 1207.

$C_{10}H_{14}O_3$ Hydroxyketodihydroepicampholenic lactone (Perkin and Titley), 1106.

$C_{10}H_{14}O_4$ Benzoyl glyceride (Fairbourne and Toms), 1040.

γ-Lactone of 1-hydroxy*cyclo*hexylethane-αβ-dicarboxylic acid, and its silver salt (Birch, Gough, and Kon), 1326.

$C_{10}H_{15}N$ Epicampholenonitrile (Perkin and Titley), 1102.

$C_{10}H_{16}O$ Epicamphor (Perkin and Titley), 1089.

*cyclo*Heptenylacetone (Kon), 827.

Piperitone (Read and Smith), 779 ; constitution of (Simonsen), 1650.

$C_{10}H_{16}O_2$ Dihydroepicampholenolactone (Perkin and Titley), 1104.

Epicampholenic acids (Perkin and Titley), 1103.

$C_{10}H_{16}O_5$ 1-Hydroxy*cyclo*hexylethane-αβ-dicarboxylic acid, silver salt (Birch, Gough, and Kon), 1327.

$C_{10}H_{17}Cl$ Hydrochloride of hydrocarbon, $C_{10}H_{16}$ (Simonsen), 1649.

$C_{10}H_{18}Br_2$ Dihydrobromide of hydrocarbon, $C_{10}H_{16}$ (Simonsen), 1650.

$C_{10}H_{19}N$ *l*-Epicamphylamine (Perkin and Titley), 1105.

$C_{10}H_{20}O_6$ Trimethyl-β-methylglucoside (Irvine and Oldham), 1758.

10 III

$C_{10}H_6O_2N$ 1:2-Naphthaquinone-1-oxime, hexamminocobaltic salt (Morgan and Smith), 708.

$C_{10}H_6O_3N$ 7-Oxy-1:2-naphthaquinone-1-oxime, pentamminodicobaltic salt (Morgan and Smith), 709.

$C_{10}H_7ONa$ Sodium-β-naphthoxide, velocity of reaction of ethyl iodide and (Cox), 149.

$C_{10}H_7O_3N$ 7-Hydroxy-1:2-naphthaquinone-1-oxime, cobaltic salt (Morgan and Smith), 708.

$C_{10}H_7Br_2Bi$ α-Naphthyldibromobismuthine (Challenger and Allpress), 919.

$C_{10}H_8O_2S$ 2-Acetyl-3-oxy(1)thionaphthen (Smiles and McClelland), 1814.

$C_{10}H_8O_4N_4$ Dinitro-2:3:6:7-dimethylenetetraoxyanthraquinonedi-imide (Keffler), 1479.

$C_{10}H_8O_5N_2$ 2:4-Dinitro-5:8-dihydro-α-naphthol (Rowe and Levin), 2028.

$C_{10}H_9O_2N$ Scatole-2-carboxylic acid (Kermack, Perkin, and Robinson), 1634.

$C_{10}H_9O_3N$ 2-Methoxy-3-cyano-*p*-toluic acid, and its silver salt (Simonsen and Rau), 1344.

6-Methoxyindole-2-carboxylic acid (Kermack, Perkin, and Robinson), 1632.

3-Methoxy-4-methyl-*o*-phthalimide (Simonsen and Rau), 1345.

Nitrodihydro-α-naphthols (Rowe and Levin), 2026.

$C_{10}H_9O_4Cl$ *m*-Chlorobenzylmalonic acid (Kenner and Witham), 1460.

$C_{10}H_{9}O_{6}N$ *o*-Nitro-*p*-methoxyphenylpyruvic acid (KERMACK, PERKIN, and ROBINSON), 1630.

$C_{10}H_{10}O_{3}Cl_{2}$ 4-Hydroxy-5-ββ-dichloroethyl-*m*-toluic acid, and its calcium salt (ALIMCHANDANI and MELDRUM), 208.

$C_{10}H_{10}O_{4}N_{2}$ 2:3:6:7-Dimethylenetetraoxyanthraquinonedi-imide (KEFFLER), 1479.

$C_{10}H_{10}O_{4}Br_{2}$ α:5-Dibromo-β-hydroxy-2-methoxy-β-phenylpropionic acid, and its brucine salt (READ and ANDREWS), 1783.

$C_{10}H_{11}ON$ 6-Methoxy-3-methylindole (KERMACK, PERKIN, and ROBINSON) 1640.

$C_{10}H_{11}OCl$ Chlorophenyl *n*-propyl ketones (MORGAN and HICKINBOTTOM), 1885.

$C_{10}H_{11}O_{2}N$ 3-Methoxy-4-ethoxybenzonitrile (KEFFLER), 1481.

$C_{10}H_{11}O_{3}N$ Nitrophenyl *n*-propyl ketones (MORGAN and HICKINBOTTOM), 1882.

$C_{10}H_{11}O_{4}N$ 3-Nitro-4-hydroxyphenyl *n*-propyl ketone (MORGAN and HICKINBOTTOM), 1888.

$C_{10}H_{11}O_{5}N$ 4-Carbethoxyamino-*m*-hydroxybenzoic acid (FROELICHER and COHEN), 1430.

$C_{10}H_{11}ClBr_{2}$ 4-Chloro-αβ-dibromo-*n*-butylbenzene (MORGAN and HICKINBOTTOM), 1887.

$C_{10}H_{12}O_{2}Br_{2}$ *cyclo*Pentane*spiro*-4:4-dibromo*cyclo*hexane-3:5-dione (NORRIS and THORPE), 1210.

$C_{10}H_{12}O_{2}S_{2}$ *cyclo*Pentane*spiro*-3:5-diketo-4-dithio*cyclo*hexane (NAIK), 1240.

$C_{10}H_{12}O_{4}N_{2}$ Acetyl derivative of 3-nitro-2-methoxy-*p*-toluidine (SIMONSEN and RAU), 1342.

$C_{10}H_{12}O_{4}N_{4}$ Acetonedinitrotolylhydrazones (BRADY and BOWMAN), 899.
n-Propaldehyde-2:4-dinitro-*m*-tolylhydrazone (BRADY and BOWMAN), 899.

$C_{10}H_{13}ON$ Aminophenyl *n*-propyl ketones, and their salts (MORGAN and HICKINBOTTOM), 1883.

$C_{10}H_{13}O_{2}Br$ *cyclo*Pentane*spiro*-4-bromo*cyclo*hexane-3:5-dione (NORRIS and THORPE), 1210.

$C_{10}H_{13}O_{2}N_{5}$ 4-Diazoamino-3:5-dimethyl*iso*oxazole (MORGAN and BURGESS), 1547.

$C_{10}H_{13}O_{3}N_{3}$ 3:5-Dimethyl*iso*oxazole-4-azo-acetylacetone (MORGAN and BURGESS), 1546.

$C_{10}H_{14}ON_{2}$ Acetyl-4:6-diamino-*m*-xylene (PEARMAN), 718.

$C_{10}H_{14}ClAs$ γ-Phenylpropylmethylchloroarsine (BURROWS and TURNER), 430.

$C_{10}H_{14}BrAs$ γ-Phenylpropylmethylbromoarsine (BURROWS and TURNER), 430.

$C_{10}H_{15}O_{4}N$ Ethyl α-cyanopropane-βγ-dicarboxylate (INGOLD), 340.

$C_{10}H_{16}O_{4}N_{4}$ 3-Nitrophenyl *n*-propyl ketone *p*-nitrophenylhydrazone (MORGAN and HICKINBOTTOM), 1882.

$C_{10}H_{16}O_{4}Br_{2}$ Ethyl dibromoadipates (INGOLD), 962.

$C_{10}H_{16}O_{4}I_{2}$ Ethyl di-iodoadipates (INGOLD), 963.

$C_{10}H_{17}ON$ Piperitoneoximes (READ and SMITH), 784; (SIMONSEN), 1651.

$C_{10}H_{17}OAs$ Phenyldimethylethylarsonium hydroxide, salts of (BURROWS and TURNER), 1450.

$C_{10}H_{17}O_{2}Cl$ Pinene chlorohydrins (HENDERSON and MARSH), 1497.

$C_{10}H_{17}O_{4}Cl$ Ethyl α-chloroadipate (INGOLD), 961.

$C_{10}H_{17}O_{4}Br$ Ethyl α-bromoadipate (INGOLD), 961.

$C_{10}H_{18}O_{2}Cl_{2}$ 1:2-Dichloromenthane-6:8-diol, or Sobrerol dichloride (HENDERSON and MARSH), 1496.
Pinene dichlorohydrins (HENDERSON and MARSH), 1495.

$C_{10}H_{20}O_2N_2$ *dl*-Piperitonehydroxylamino-oxime (Read and Smith), 788.

$C_{10}H_{21}ON$ 1-*iso*Butoxymethylpiperidine, preparation of (McLeod and Robinson), 1474.

10 IV

$C_{10}H_6O_8NS_2$ 8-Oxy-1:2-naphthaquinone-2-oxime-3:6-disulphonic acid, pentamminocobaltic salts (Morgan and Smith), 713.

$C_{10}H_7O_5NS$ 1:2-Naphthaquinone-2-oxime-4-sulphonic acid, cobaltic and β-naphthylamine salts (Morgan and Smith), 710.

$C_{10}H_7O_8NS_2$ 8-Hydroxy-1:2-naphthaquinone-2-oxime-3:6-disulphonic acid, cobaltic and β-naphthylamine salts (Morgan and Smith), 713.

$C_{10}H_9O_2N_2I$ 6-Nitroquinoline methiodide (Hamer), 1435.

$C_{10}H_{10}ON_3Cl$ Chloro-1-hydrindone semicarbazones (Kenner and Witham), 1459.

$C_{10}H_{10}O_2N_2S_2$ Dithiomesoxomono-*p*-toluidide (Naik), 1237.

$C_{10}H_{10}O_3NCl$ 4-Chloro-3-nitrophenyl *n*-propyl ketone (Morgan and Hickinbottom), 1887.

$C_{10}H_{12}ONCl$ 4-Chloro-3-aminophenyl *n*-propyl ketone, and its hydrochloride (Morgan and Hickinbottom), 1888.

$C_{10}H_{12}O_2N_3Br$ 5-Bromo-2-methoxyphenylacetaldehyde semicarbazone (Read and Andrews), 1785.

$C_{10}H_{12}O_7N_3Tl$ Thalliumdiethyl 2:4:6-trinitrophenoxide (Goddard), 1313.

$C_{10}H_{13}O_5N_2Tl$ Thalliumdiethyl 2:4-dinitrophenoxide (Goddard), 1313.

$C_{10}H_{14}O_3NTl$ Thalliumdiethyl nitrophenoxides (Goddard), 1312.

$C_{10}H_{14}O_5N_3Tl$ Thalliumdiethyl 4:6-dinitro-2-aminophenoxide (Goddard), 1313.

$C_{10}H_{17}ONBr_2$ Dibromopiperitoneoxime (Simonsen), 1652.

$C_{10}H_{17}ON_2I$ Substance, from eseroline methiodide, methyl iodide, and sodium ethoxide (Stedman), 892.

10 VI

$C_{10}H_{20}O_7N_4BrS_2Co$ *cis*-Bromobenzene-3:4-disulphonatodiethylenediaminecobaltic hydroxide, salts of (Duff), 1986.

C_{11} Group.

$C_{11}H_8O_3$ Dihydroxynaphthaldehydes (Morgan and Vining), 177.

$C_{11}H_8O_4$ Substance, from sodium and phenyl acetate (Perkin), 1289.

$C_{11}H_8N_2$ Norharman, and its salts (Kermack, Perkin, and Robinson), 1602.

$C_{11}H_{10}O_7$ 4:5-Dimethoxy-*o*-phthalonic acid (+ $2H_2O$) and its acid calcium salt (Fargher and Perkin), 1735.

$C_{11}H_{12}O_2$ *o*-Methoxystyryl methyl ketone (Heilbron and Buck), 1509.

$C_{11}H_{12}O_5$ Methyl *m*-opianates (Fargher and Perkin), 1741.

$C_{11}H_{14}O_2$ *dl-trans-cyclo*Pentane-1:3-dicarboxylic acid, resolution of (Perkin and Scarborough), 1400.

$C_{11}H_{14}O_5$ Ethyl 6-ethoxy-3-methyl-2-pyrone-5-carboxylate (Ingold and Perren), 1601.

$C_{11}H_{14}O_6$ Lactone of 1-hydroxy*cyclo*hexylethane-αββ-tricarboxylic acid (Birch, Gough, and Kon), 1326.

$C_{11}H_{14}N_2$ 1:4-*endo*Ethylene-6-methyltetrahydroquinoxaline, and its salts (Moore and Doubleday), 1174.

$C_{11}H_{16}O_2$ Hydroxymethylene-*l*-epicamphor (Perkin and Thorpe), 1096.

$C_{11}H_{16}O_4$ *cyclo*Hexane*spirocyclo*hexane-3:5-dione (Norris and Thorpe), 1205.

$C_{11}H_{16}O_5$ Ethyl *cyclo*pentanonedicarboxylate (Ingold), 349; (Ingold and Thorpe), 499.

$C_{11}H_{17}O_7$ 1-Hydroxy*cyclo*hexylethane-αββ-tricarboxylic acid, silver salt (Birch, Gough, and Kon), 1326.

$C_{11}H_{17}As$ γ-Phenylpropyldimethylarsine (BURROWS and TURNER), 429.

$C_{11}H_{18}O_7$ Ethyl trimethyl saccharolactone (IRVINE and OLDHAM), 1757.

11 III

$C_{11}H_7O_3N$ 2-Carboxyindole-3-acetic anhydride (KERMACK, PERKIN, and ROBINSON), 1623.

$C_{11}H_7O_4N$ 1:2-Naphthaquinone-1-oxime-3-carboxylic acid, cobaltic salts (MORGAN and SMITH), 709.

$C_{11}H_7O_6N_3$ 2-*m*-Nitrophenylglyoxaline-4:5-dicarboxylic acid (FARGHER), 163.

$C_{11}H_8ON_2$ 5-Keto-4:5-dihydroindolediazine(1:4) (KERMACK, PERKIN, and ROBINSON), 1627.

$C_{11}H_8O_2N_2$ Norharmol (KERMACK, PERKIN, and ROBINSON), 1619.

$C_{11}H_8O_3S$ (1)Thionaphtha-4-oxycoumarin (SMILES and McCLELLAND), 1815.

$C_{11}H_9O_4N$ 2-Carboxyindole-3-acetic acid (KERMACK, PERKIN, and ROBINSON), 1622.

$C_{11}H_9O_4N_3$ 2-*m*-Aminophenylglyoxaline-4:5-dicarboxylic acid (FARGHER), 163.

$C_{11}H_{10}O_3N_2$ 2-Carboxyindole-3-acetamide (KERMACK, PERKIN, and ROBINSON), 1623.

$C_{11}H_{10}O_3N_4$ 5-Nitro-*p*-acetylaminophenylglyoxaline (GRANT and PYMAN), 1902.

$C_{11}H_{10}O_4N_2$ Dimethyldiketotetrahydroquinazolinecarboxylic acid (SCOTT and COHEN), 668.

$C_{11}H_{11}O_2N$ 1:3-Dimethylindole-2-carboxylic acid (KERMACK, PERKIN, and ROBINSON), 1636.

3-Methoxy-4-methyl-α-quinolone (KERMACK, PERKIN, and ROBINSON), 1635.

$C_{11}H_{11}O_2N_3$ 1-*p*-Nitrophenyl-3:5-dimethylpyrazole (MORGAN and DREW), 621.

$C_{11}H_{11}O_3N$ 6-Methoxy-3-methylindole-2-carboxylic acid (KERMACK, PERKIN, and ROBINSON), 1640.

$C_{11}H_{11}O_3N_3$ 3:5-Dimethyl*iso*oxazole-4-azoresorcinol (MORGAN and BURGESS), 703.

$C_{11}H_{12}O_2N_2$ *cyclo*Hexane*spiro*-2:3-dicyano*cyclo*propane-2-carboxylic acid (BIRCH, GOUGH, and KON), 1325.

$C_{11}H_{12}O_3N_2$ Acetylacetone-*p*-nitroanil (MORGAN and DREW), 624.

$C_{11}H_{12}O_4N_2$ 1-*p*-Nitroanilinoacetylacetone (MORGAN and DREW), 623.

$C_{11}H_{13}ON_3$ *cyclo*Hexane*spiro*-2:3-dicyano*cyclo*propane-2-carboxylamide (BIRCH, GOUGH, and KON), 1324.

$C_{11}H_{13}O_2N$ *o*-Methoxystyrylmethyl ketoxime (HEILBRON and BUCK), 1509.

$C_{11}H_{13}O_5N$ Carbethoxyamino-*m*-methoxybenzoic acids (FROELICHER and COHEN), 1431.

$C_{11}H_{13}O_5N_3$ Acetyl derivative of 4-nitro-2-carbethoxyphenylhydrazine (KENNER and WITHAM), 1055.

$C_{11}H_{14}O_2N_2$ Methylmalonomono-*o*-toluidide (NAIK), 1238.

$C_{11}H_{14}O_2Cl_2$ *cyclo*Hexane*spiro*-4:4-dichloro*cyclo*hexane-3:5-dione (NORRIS and THORPE), 1209.

$C_{11}H_{14}O_2Br_2$ *cyclo*Hexane*spiro*-4:4-dibromo*cyclo*hexane-3:5-dione (NORRIS and THORPE), 1209.

$C_{11}H_{14}O_4N_4$ *n*-Butaldehyde-2:4-dinitro-*m*-tolylhydrazone (BRADY and BOWMAN), 899.

Methyl ethyl ketone 2:4-dinitro-*m*-tolylhydrazone (BRADY and BOWMAN), 899.

$C_{11}H_{15}O_2Cl$ *cyclo*Hexane*spiro*-4-chloro*cyclo*hexane-3:5-dione (NORRIS and THORPE), 1209.

$C_{11}H_{15}O_2Br$ *cyclo*Hexane*spiro*-4-bromo*cyclo*hexane-3:5-dione (NORRIS and THORPE), 1208.

$C_{11}H_{15}O_3N$ 4:5-Dimethoxy-*o*-tolyl methyl ketoxime (FARGHER and PERKIN), 1732.

$C_{11}H_{15}O_3N_3$ 5-Hydroxy-4-methoxy-*o*-tolyl methyl ketone semicarbazone (FARGER and PERKIN), 1733.

$C_{11}H_{15}O_4N$ Ethyl α-cyano-γ-methylglutaconate (INGOLD and PERREN), 1597.

$C_{11}H_{16}IAs$ *As*-Methyltetrahydroarsinoline methiodide (BURROWS and TURNER), 431.

$C_{11}H_{17}ON$ Amino methylene-epicamphor (PERKIN and TITLEY), 1101.

$C_{11}H_{17}O_4N$ Ethyl cyanomethylglutarates (INGOLD), 338; (INGOLD and THORPE), 500.

$C_{11}H_{17}O_4N_3$ Semicarbazone of acid, $C_{10}H_{14}O_4$, from oxidation of *l*-epicampholenic acid (PERKIN and TITLEY), 1107.

$C_{11}H_{18}O_4Br_2$ *iso*Propyl αα′-dibromoglutarate (INGOLD), 318.

$C_{11}H_{19}ON_3$ *cyclo*Heptenylacetone semicarbazone (KON), 827.
  Piperitone semicarbazones (READ and SMITH), 784; (SIMONSEN), 1650.

$C_{11}H_{22}O_2N_2$ Malondi-*n*- and -*iso*-butylamides (BACKES, WEST, and WHITELEY), 368.

11 IV

$C_{11}H_7O_4N_2Cl$ 6(7)-Chloro-7(6)-methylquinoxaline-2:3-dicarboxylic acid (+ $2H_2O$) (MORGAN and CHALLENOR), 1540.

$C_{11}H_7O_4N_4Br$ 2-*p*-Bromobenzeneazoglyoxaline-4:5-dicarboxylic acid (FARGHER), 162.

$C_{11}H_9O_2N_4Br$ 4-*p*-Bromobenzeneazo-2-methylglyoxaline-5-carboxylic acid (FARGHER), 161.

$C_{11}H_9O_4N_4Br$ 2-*p*-Bromobenzenehydrazoglyoxaline-4:5-dicarboxylic acid (FARGHER), 163.

$C_{11}H_{11}O_2N_2Br$ *p*-Bromobenzeneazoacetylacetone (MORGAN and DREW), 622.

$C_{11}H_{11}O_2N_2I$ 6-Nitroquinaldine methiodide (HAMER), 1435.

$C_{11}H_{14}O_2ClBr$ *cyclo*Hexane*spiro*-4-chloro-4-bromo*cyclo*-hexane-3:5-dione (NORRIS and THORPE), 1210.

$C_{11}H_{16}O_3NTl$ Thalliumdiethyl nitrotolyloxides (GODDARD), 1314.

$C_{11}H_{20}O_2N_2Br_2$ Dibromomalondi*iso*butylamide (BACKES, WEST, and WHITELEY), 370.

$C_{11}H_{21}O_2N_2Br$ Bromomalondi-*n*- and -*iso*-butylamides (BACKES, WEST, and WHITELEY), 368.

11 V

$C_{11}H_{21}O_6N_4SCo$ *cis*-*o*-Sulphobenzoacetatodiethylenediaminecobaltic hydroxide, salts of (DUFF), 1985.

11 VI

$C_{11}H_{20}O_5N_4BrSCo$ *cis*-*o*-Sulphobenzoacetatodiethylenediaminecobaltic bromide (+ H_2O) (DUFF), 1985.

C_{12} Group.

$C_{12}H_9N$ Carbazole, oxidation of (PERKIN and TUCKER), 216; additive compound of 4′-dimethylamino-2-hydroxydistyrylketone with (HEILBRON and BUCK), 1512.

$C_{12}H_{10}N_2$ Harmine (KERMACK, PERKIN, and ROBINSON), 1602.

$C_{12}H_{13}N$ 6-Ethylquinaldine (MILLS, HARRIS, and LAMBOURNE), 1300.
  Tetrahydrocarbazole, and its picrate (PERKIN and PLANT), 1831.

$C_{12}H_{14}O_4$ Acetyl derivative of 5-hydroxy-4-methoxy-*o*-tolyl methyl ketone (Fargher and Perkin), 1733.

$C_{12}H_{14}N_2$ 6-Aminotetrahydrocarbazole (Perkin and Plant), 1833.

$C_{12}H_{16}N_2$ 1:4-*endo*Trimethylene-6-methyltetrahydroquinoxaline, and its salts (Moore and Doubleday), 1174.

$C_{12}H_{18}O_6$ Ethyl aconitate, preparation of (Ingold), 850.

$C_{12}H_{20}O_6$ Ethyl α-acetoxyadipate (Ingold), 966.

$C_{12}H_{22}O_{11}$ Cellobiose, constitution of (Haworth and Hirst), 193.

12 III

$C_{12}H_6Cl_2S_4$ Substance, from chlorobenzene and sulphur chloride (Rây), 1963.

$C_{12}H_8O_3N_2$ Norharmolcarboxylic acid, and its sulphate (Kermack, Perkin, and Robinson), 1618.

$C_{12}H_8O_4Cl_6$ 6-Methyl-2:4-bistrichloromethyl-1:3-benzdioxine-8-carboxylic acid, and its sodium salt (Alimchandani and Meldrum), 208.

$C_{12}H_{10}ON_2$ 5-Keto-7-methyl-4:5-dihydroindolediazine(1:4) (Kermack, Perkin, and Robinson), 1635.

2-Keto-1-methyl-2:3-dihydronorharman (Kermack, Perkin, and Robinson), 1638.

$C_{12}H_{10}O_2N_2$ 11-Methoxy-5-keto-4:5-dihydroindolediazine(1:4) (Kermack, Perkin, and Robinson), 1633.

$C_{12}H_{10}O_3N_2$ *cyclo*Hexane*spiro*-2:3-dicyano*cyclo*propane-2:3-dicarboxylic anhydride (Birch, Gough, and Kon), 1328.

$C_{12}H_{10}N_2S_2$ Diaminothianthren (Rây), 1964.

$C_{12}H_{11}O_3N_3$ 4-Nitrobenzylideneamino-3:5-dimethyl*iso*oxazoles (Morgan and Burgess), 701.

$C_{12}H_{11}O_5N$ 6-Methoxy-2-carboxyindole-3-acetic acid (Kermack, Perkin, and Robinson), 1641.

$C_{12}H_{12}ON_2$ Acetylaminoquinaldines (Hamer), 1438.

4-Benzylideneamino-3:5-dimethyl*iso*oxazole (Morgan and Burgess), 701.

$C_{12}H_{12}O_2N_2$ 4-Benzoylamino-3:5-dimethyl*iso*oxazole (Morgan and Burgess), 701.

$C_{12}H_{12}O_3N_4$ 4-*p*-Nitrobenzylidenehydrazino-3:5-dimethyl*iso*oxazole (Morgan and Burgess), 1548.

$C_{12}H_{12}O_4N_2$ *cyclo*Hexane*spiro*-2:3-dicyano*cyclo*propane-2:3-dicarboxylic acid (Birch, Gough, and Kon), 1327.

Methyl dimethyldiketotetrahydroquinazolinecarboxylate (Scott and Cohen), 669.

$C_{12}H_{13}O_2N$ Ethyl α-keto-β-*o*-nitrophenylbutyrate (Kermack, Perkin, and Robinson), 1684.

$C_{12}H_{13}O_6N$ *cyclo*Hexane*spiro*-2-cyano*cyclo*propane-2:3:3-tricarboxylic acid (Birch, Gough, and Kon), 1328.

$C_{12}H_{14}ON_2$ Acetyl derivative from base $C_{20}H_{24}N_2$ (Pearman), 720.

$C_{12}H_{14}O_5N_2$ 2:6-Dinitro-*m*-4-xylyl *n*-propyl ketone (Morgan and Hickinbottom), 1891.

$C_{12}H_{15}OCl$ 6-Chloro-*m*-4-xylyl *n*-propyl ketone (Morgan and Hickinbottom), 1891.

$C_{12}H_{15}O_2N$ 3-Acetylaminophenyl *n*-propyl ketone (Morgan and Hickinbottom), 1888.

$C_{12}H_{15}O_3N$ Nitro-*m*-4-xylyl *n*-propyl ketones (Morgan and Hickinbottom), 1890.

$C_{12}H_{17}ON$ 6-Amino-*m*-4-xylyl *n*-propyl ketone, and its salts (Morgan and Hickinbottom), 1890.

$C_{12}H_{17}O_4N_3$ 2:4-Dinitro-β-diethylaminoethylbenzene, and its salts (McLeod and Robinson), 1476.

$C_{12}H_{19}O_2N_3$ Hydroxymethylene-epicamphorsemicarbazone (Perkin and Titley), 1099.

$C_{12}H_{19}O_5N_3$ Semicarbazone of ethyl *cyclo*pentanone-2:4-dicarboxylate (Ingold and Thorpe), 500.

$C_{12}H_{20}O_6N_2$ Ethyl αα′-dicarbamyl-β-methylglutarate (Gupta), 304.

$C_{12}H_{20}IAs$ γ-Phenylpropyldimethylarsine methiodide (Burrows and Turner), 429.

$C_{12}H_{22}O_4S_3$ Diacetyl derivative of sulphidobis-β-hydroxydiethyl sulphide (Bennett and Whincop), 1863.

$C_{12}H_{23}O_3N_3$ Ethyl *l*-γ-acetyl-α-*iso*propylbutyrate semicarbazone (Simonsen), 1653.

$C_{12}H_{24}O_4N_2$ Piperitonehydroxylamino-oximes (Simonsen), 1651.

12 IV

$C_{12}H_6O_4Cl_2S_2$ Substance, from oxidation of dichlorothianthren (Rây), 1962.

$C_{12}H_8O_6N_2Ba$ Barium nitrophenoxides (Goddard), 1162.

$C_{12}H_8O_6N_2Ca$ Calcium nitrophenoxides (Goddard), 1164.

$C_{12}H_8O_6N_2Sr$ Strontium nitrophenoxides (Goddard), 1163.

$C_{12}H_{10}O_6N_2S$ 6-Acetylamino-1:2-naphthaquinone-2-oxime-3-sulphonic acid, cobaltic and β-naphthylamine salts (Morgan and Smith), 711.

$C_{12}H_{11}O_2N_2Cl$ 8-Chloro-5-nitrotetrahydrocarbazole (Perkin and Plant), 1837.

$C_{12}H_{11}O_9N_2S_2$ 8-Acetylamino-1:2-naphthaquinone-2-oxime-3:6-disulphonic acid, pentamminocobaltic salt (Morgan and Smith), 712.

$C_{12}H_{12}O_2NCl$ Ethyl 7-chloro-1-iminohydrindene-2-carboxylate (Kenner and Witham), 1459.

$C_{12}H_{13}O_2Cl_3Te$ Tellurium *O*-ethylbenzoylacetone trichloride (Morgan and Drew), 618.

$C_{12}H_{13}O_3NS_2$ Ethyl dithiomesoxotolylamates (Naik), 1237.

$C_{12}H_{14}O_2N_3Cl$ *cyclo*Hexanone-2-chloro-5-nitrophenylhydrazone (Perkin and Plant), 1837.

$C_{12}H_{21}O_5N_4Co$ *cis*-Phthalatodiethylenediaminecobaltic hydroxide, salts of (Duff), 1984.

$C_{12}H_{26}O_4N_4S_2$ Methylmalonodimethylamide disulphide (Naik), 1239.

12 V

$C_{12}H_{12}O_4N_2SAs_2$ 3:3′-Diamino-4:4′-dihydroxy-5-sulphinoarsenobenzene, hydrochloride of (King), 1115.

$C_{12}H_{12}O_5N_2SAs_2$ 3:3′-Diamino-4:4′-dihydroxy-5-sulphoarsenobenzene, hydrochloride of (King), 1117.

$C_{12}H_{12}O_6N_2S_2As_2$ 3:3′-Diamino-4:4′-dihydroxy-5:5′-disulphinoarsenobenzene (King), 1113.

$C_{12}H_{12}O_7N_2S_2As_2$ 3:3′-Diamino-4:4′-dihydroxy-5-sulpho-5′-sulphinoarsenobenzene (King), 1118.

$C_{12}H_{12}O_8N_2S_2As_2$ 3:3′-Diamino-4:4′-dihydroxy-5:5′-disulphoarsenobenzene (King), 1116.

$C_{12}H_{20}O_4N_4BrCo$ *cis*-Phthalatodiethylenediaminecobaltic bromide (+ $3H_2O$) (Duff), 1984.

C_{13} Group.

$C_{13}H_{10}$ Fluorene, additive compounds of 4′-dimethylamino-2-hydroxydistyryl ketone with (Heilbron and Buck), 1511.

13 II

$C_{13}H_{10}O$ Benzophenone, additive compounds of 4′-dimethylamino-2-hydroxydistyryl ketone with (HEILBRON and BUCK), 1513.

$C_{13}H_{14}O_3$ *ac*-1-Keto-3-methyltetrahydronaphthyl-3-acetic acid, and its silver salt (KON and STEVENSON), 90.

$C_{13}H_{15}N$ 9-Methyltetrahydrocarbazole (PERKIN and PLANT), 1834.

$C_{13}H_{16}N_2$ 6-Amino-9-methyltetrahydrocarbazole, and its picrate (PERKIN and PLANT), 1835.

$C_{13}H_{18}O_4$ Ethyl *cyclo*pentane*spirocyclo*hexane-3:5-dione-2-carboxylate (+ H_2O) (NORRIS and THORPE), 1207.

$C_{13}H_{18}O_3$ 1-Keto-3-methyloctahydronaphthyl-3-acetic acid, and its silver salt (KON and STEVENSON), 92.

13 III

$C_{13}H_5O_6Cl_9$ Lactone of 7:8-dihydroxy-2:4-bistrichloromethyl-6-*β*-trichloro-*α*-hydroxyethyl-1:3-benzdioxine-5-carboxylic acid (ALIMCHANDANI and MELDRUM), 206.

$C_{13}H_9O_3N_3$ Nitro-3-keto-2-phenyl-1:3-dihydroindazoles, and their sodium salts (KENNER and WITHAM), 1056.

$C_{13}H_9O_5N_3$ *p*-Nitrobenzaldoxime-*N*-*p*-nitrophenyl ether (BARROW and GRIFFITHS), 216.

$C_{13}H_{10}O_3N_2$ Acetyl derivative of 2-carboxyindole-3-acetimide (KERMACK, PERKIN, and ROBINSON), 1624.

p-Nitrobenzaldoxime-*N*-phenyl ether (BARROW and GRIFFITHS), 213.

$C_{13}H_{10}N_3Cl$ 6-Chloro-3-phenyl-3:4-tolylenediazoimine (MORGAN and JONES), 191.

$C_{13}H_{13}O_4N$ Dimethyl 2-carboxyindole-3-acetate (KERMACK, PERKIN, and ROBINSON), 1623.

$C_{13}H_{13}N_2Cl$ 6-Chloro-3-phenyl-3:4-tolylenediamine (MORGAN and JONES), 191.

$C_{13}H_{13}N_4Cl$ Benzene-5-azo-6-chloro-2:4-tolylenediamine, and its dihydrochloride (MORGAN and JONES), 188.

$C_{13}H_{14}ON_2$ Harmaline (KERMACK, PERKIN, and ROBINSON), 1602.

$C_{13}H_{14}O_2N_2$ 6-Nitro-9-methyltetrahydrocarbazole (PERKIN and PLANT), 1834.

$C_{13}H_{14}O_9N_2$ Diacetyl derivative of glycerol *α*-2:4-dinitrophenyl ether (FAIRBOURNE and TOMS), 1037.

$C_{13}H_{15}O_3N$ Ethyl 6-methoxy-3-methylindole-2-carboxylate (KERMACK, PERKIN, and ROBINSON), 1640.

$C_{13}H_{15}O_6N$ Ethyl *α*-keto-*β*-*o*-nitro-*p*-methoxyphenylbutyrate (KERMACK, PERKIN, and ROBINSON), 1639.

$C_{13}H_{16}O_3N_2$ Methyl ether of 4-*p*-hydroxybenzylhydantoin *OO*-dimethyl ether (SCOTT and COHEN), 671.

$C_{13}H_{16}O_5N_2$ *p*-Nitroanilino-ethoxyacetone (MORGAN and DREW), 623.

$C_{13}H_{16}NI$ 6-Ethylquinaldine methiodide (MILLS, HARRIS, and LAMBOURNE), 1300.

$C_{13}H_{17}O_6N$ Ethyl *α*-cyano-*γ*-carboxyglutaconate, and its metallic salts (INGOLD and PERREN), 1594.

$C_{13}H_{19}ON$ *β*-Diethylaminopropiophenone, and its salts (MCLEOD and ROBINSON), 1475.

$C_{13}H_{30}O_2N_2$ Di(diethylaminomethyl)trimethylene ether (MCLEOD and ROBINSON), 1473.

13 IV

$C_{13}H_8O_2N_3Cl$ 3-Chloro-5-nitro-2-phenylindazole (KENNER and WITHAM), 1057.

$C_{13}H_{10}O_3N_3Cl$ Chloronitrophenyltolylnitrosoamines (Morgan and Jones), 190.

$C_{13}H_{11}O_2N_2Cl$ Chloronitro-*N*-phenyltoluidines (Morgan and Jones), 190; (Morgan and Glover), 1704.

$C_{13}H_{11}O_3NS_4$ Ethyl γ-phenylcarbamyl-*αγ*-bisdisulphidoacetoacetate (Naik), 1241.

$C_{13}H_{12}O_2N_2S$ Benzenediazo-*p*-toluenesulphinate (Dutt, Whitehead, and Wormall), 2089.

$C_{13}H_{12}O_2N_5Cl$ 4′-Nitrobenzene-5-azo-6-chloro-2:4-tolylenediamine (Morgan and Jones), 188.

$C_{13}H_{15}ON_2I$ Acetylaminoquinaldine methiodides (Hamer), 1438.

$C_{13}H_{22}ONBr$ α-Bromopropiono-*d*-bornylamide (Shimomura and Cohen), 1822.

$C_{13}H_{23}O_5N_4Co$ *cis*-Homophthalatodiethylenediaminecobaltic hydroxide, salts of (Duff), 1986.

13 V

$C_{13}H_{25}O_6N_4SCo$ *cis*-Benzylsulphoacetatodiethylenediaminecobaltic hydroxide, salts of (Duff), 1985.

13 VI

$C_{13}H_{24}O_5N_4BrSCo$ *cis*-Benzylsulphoacetatodiethylenediaminecobaltic bromide (+ $3H_2O$) (Duff), 1985.

C_{14} Group.

$C_{14}H_{10}$ Phenanthrene, additive compound of 4′-dimethylamino-2-hydroxydistyryl ketone with (Heilbron and Buck), 1511.

$C_{14}H_{12}$ 9:10-Dihydrophenanthrene, preparation of (Henstock), 1461.

$C_{14}H_{22}$ 1:4-Di-*n*-butylbenzene (Morgan and Hickinbottom), 1892.

14 II

$C_{14}H_6O_8$ Ellagic acid, formation of, from gallotannin (Nierenstein, Spiers, and Geake), 275.

$C_{14}H_8Br_2$ Dibromophenanthrene (Henstock), 57.

$C_{14}H_9Br_3$ Bromophenanthrene dibromide (Henstock), 57.

$C_{14}H_{10}O_3$ 1-Hydroxy-3-methylxanthone, and its potassium derivative (Perkin), 1291.

$C_{14}H_{12}N_2$ 1:10-Dimethyl-5:6-naphtha*iso*diazine (Kenner and Stubbings), 602.

$C_{14}H_{16}O_3$ *ac*-1-Keto-3-ethyltetrahydronaphthyl-3-acetic acid, and its silver salt (Kon and Stevenson), 92.

$C_{14}H_{16}N_2$ 6:6′-Diamino-2:2′-ditolyl (Kenner and Stubbings), 600.

$C_{14}H_{20}O_4$ Ethyl *cyclo*hexane*spirocyclo*hexane-3:5-dione-2-carboxylate (+ H_2O) (Norris and Thorpe), 1204.

$C_{14}H_{23}N$ 2-Amino-1:4-di-*n*-butylbenzene, and its salts (Morgan and Hickinbottom), 1892.

14 III

$C_{14}H_8OBr_2$ Dibromophenanthrone (Henstock), 58.

$C_{14}H_8O_2N_2$ Dilactam of γ-6:6′-diaminodiphenic acid (Kenner and Stubbings), 601.

$C_{14}H_8O_4S_2$ Thianthrendicarboxylic acid (Rây), 1966.

$C_{14}H_8O_6N_4$ "Hydrazide" of γ-6:6′-dinitrodiphenic acid (Kenner and Stubbings), 600.

$C_{14}H_8O_8N_2$ γ-6:6′-Dinitrodiphenic acid, and its salts (Kenner and Stubbings), 593.

$C_{14}H_9O_5N$ Nitro-1-hydroxy-3-methylxanthones (Perkin), 1293.

$C_{14}H_9NBr_2$ Dibromo-9-aminophenanthrene (Henstock), 59.

$C_{14}H_{10}OCl_2$ Diphenylchloroacetyl chloride, action of magnesium phenyl haloids on (McKenzie and Boyle), 1131.

$C_{14}H_{10}O_4S_2$ *m*-Dithiobenzoic acid (Smiles and Stewart), 1792.

$C_{14}H_{10}O_6N_4$ γ-6:6′-Dinitrodiphenamide (Kenner and Stubbings), 599.

$C_{14}H_{10}O_6S_2$ Benzoic acid *m*-disulphoxide (Smiles and Stewart), 1797.

$C_{14}H_{10}N_4S$ 4′-Triazo-1-phenyl-5-methylbenzothiazole (Morgan and Webster), 1074.

$C_{14}H_{10}Cl_2S_2$ Dichlorodimethylthianthren (Rây), 1963.

$C_{14}H_{11}N_2Cl$ 5-Chloro-1-phenyl-6-methylbenziminazole (Morgan and Challenor), 1543.

$C_{14}H_{12}ON_2$ Phenylglyoxalphenylhydrazone, preparation, tautomerism, and solubility of (Sidgwick and Ewbank), 487.

$C_{14}H_{12}O_4N_4$ Benzaldehydedinitrotolylhydrazones (Brady and Bowman), 899.

$C_{14}H_{13}O_4N_3$ 6-Nitro-*m*-xylene-4-azoresorcinol (Pearman), 717.

$C_{14}H_{14}O_2N_2$ Diamide of αα′-dicyano-β-benzylglutaric acid (Kon and Stevenson), 93.

$C_{14}H_{14}O_3N_2$ 5- and 6-Nitro-9-acetyltetrahydrocarbazoles (Perkin and Plant), 1832.

$C_{14}H_{14}O_6N_2$ *p*-Nitrobenzoyl derivative of β-hydroxy-β-3:4-methylenedioxyphenylethylamine (Mason), 1080.

$C_{14}H_{14}ClBi$ Di-*p*-tolylchlorobismuthine (Challenger and Allpress), 917.

$C_{14}H_{15}ON$ 9-Acetyltetrahydrocarbazole (Perkin and Plant), 1831.

$C_{14}H_{15}O_3N_3$ Benzoyl derivative of α-methylamino-β-glyoxaline-4-propionic acid (+ ½H_2O) (Fargher and Pyman), 738.

$C_{14}H_{16}ON_2$ 6-Acetylaminotetrahydrocarbazole (Perkin and Plant), 1833.

$C_{14}H_{16}O_3N_2$ Indole-2-carboxy-α-(carbethoxy)ethylamide (Kermack, Perkin, and Robinson), 1628.

$C_{14}H_{16}O_4Cl$ Ethyl *m*-chlorobenzylmalonate (Kenner and Witham), 1460.

$C_{14}H_{16}O_{11}N_2$ 4-*p*-Acetoxybenzylhydantoin *OO*-dimethyl ether (Scott and Cohen), 671.

$C_{14}H_{17}O_3N_3$ Semicarbazone of *ac*-1-keto-3-methyltetrahydronaphthyl-3-acetic acid (Kon and Stevenson), 91.

$C_{14}H_{17}N_2I$ Phenylbenzylmethylazonium iodide, additive compound of thiocarbamide and (Singh and Lal), 211.

$C_{14}H_{17}N_4Cl_2$ 3:7-Diamino-8-methylphenazine methochloride (Cohen and Crabtree), 2068.

$C_{14}H_{19}ON_3$ *cyclo*Hexanone-*p*-acetylaminophenylhydrazone (Perkin and Plant), 1833.

$C_{14}H_{19}O_2N$ 6-Acetylamino-*m*-4-xylyl *n*-propyl ketone (Morgan and Hickinbottom), 1890.

$C_{14}H_{21}O_2N$ 2-Nitro-1:4-di-*n*-butylbenzene (Morgan and Hickinbottom), 1892.

$C_{14}H_{21}O_3N_3$ Semicarbazone of 1-keto-3-methyloctahydronaphthyl-3-acetic acid (Kon and Stevenson), 93.

$C_{14}H_{21}O_6N$ Ethyl ω-cyanomethanetriacetate (Ingold), 340, 352.

14 IV

$C_{14}H_6O_6N_2Cl_2$ Chloride of γ-6:6′-dinitrodiphenic acid (Kenner and Stubbings), 599.

$C_{14}H_7O_2NBr_2$ Dibromo-9-nitrophenanthrene (Henstock), 58.

$C_{14}H_9ONBr_2$ Dibromophenanthroneoxime (Henstock), 58.

$C_{14}H_{10}O_4NCl$ Benzoyl derivative of 2-chloro-5-nitro-*p*-cresol (Davies), 867.

$C_{14}H_{10}O_{10}N_4Cd$ Cadmium dinitrotolyloxides (D. and A. E. GODDARD), 2048.

$C_{14}H_{10}O_{10}N_4Mg$ Magnesium dinitrotolyloxides (D. and A. E. GODDARD), 2048.

$C_{14}H_{10}O_{10}N_4Sr$ Strontium dinitrotolyloxides (D. and A. E. GODDARD), 2047.

$C_{14}H_{10}O_{10}N_4Zn$ Zinc dinitrotolyloxides (D. and A. E. GODDARD), 2048.

$C_{14}H_{10}NClS$ 4′-Chloro-1-phenyl-5-methylbenzothiazole (MORGAN and WEBSTER), 1074.

$C_{14}H_{11}ON_3S$ 1-Phenyl-5-methylbenzothiazole-4′-diazonium hydroxide, salts of (MORGAN and WEBSTER), 1073, 1076.

$C_{14}H_{11}O_3N_3S_2$ 1-Phenyl-5-methylbenzothiazole-4′-diazosulphonic acid, sodium salts (MORGAN and WEBSTER), 1075.

$C_{14}H_{12}O_2N_2S$ *N*-Sulphidobisbenzamide (NAIK), 1168.

$C_{14}H_{12}O_4N_2S_2$ Disulphidobis-salicylamide (NAIK), 1169.

$C_{14}H_{12}O_6N_2Ba$ Barium nitrotolyloxides (D. and A. E. GODDARD), 2046.

$C_{14}H_{12}O_6N_2Ca$ Calcium nitrotolyloxides (D. and A. E. GODDARD), 2046.

$C_{14}H_{12}O_6N_2Mg$ Magnesium nitrotolyloxides (D. and A. E. GODDARD), 2047.

$C_{14}H_{12}O_6N_2Sr$ Strontium nitrotolyloxides (D. and A. E. GODDARD), 2046.

$C_{14}H_{18}O_4NBr$ Ethyl ester of α-bromopropionyl-*l*-tyrosine (SHIMOMURA and COHEN), 1823.

C_{15} Group.

$C_{15}H_{10}O_4$ 1:6-Dihydroxy-2-methylanthraquinone (SIMONSEN and RAU), 1339.

$C_{15}H_{12}O_2$ 9-Acetoxyfluorene, preparation of (HENSTOCK), 1463.

$C_{15}H_{12}O_3$ 1-Hydroxy-3-methylxanthone methyl ether (PERKIN), 1292.

$C_{15}H_{14}O_6$ Catechin, constitution of (NIERENSTEIN), 164.

2:4:6:3′:4′-Pentahydroxy-3-phenylchroman (NIERENSTEIN), 169.

15 III

$C_{15}H_4O_6Cl_{12}$ Lactone of 7:8-βββ-trichloroethylidenedioxy-2:4-bistrichloromethyl-6-βββ-trichloro-α-hydroxyethyl-1:3-benzdioxine-5-carboxylic acid (ALIMCHANDANI and MELDRUM), 208.

$C_{15}H_9O_6Cl_6$ Lactone of 7:8-dimethoxy-2:4-bistrichloromethyl-6-β-trichloro-α-hydroxyethyl-1:3-benzdioxine-5-carboxylic acid (ALIMCHANDANI and MELDRUM), 207.

$C_{15}H_{10}N_2S$ 4′-Cyano-1-phenyl-5-methylbenzothiazole (MORGAN and WEBSTER), 1076.

$C_{15}H_{11}O_6Cl_3$ 3:4:5-Triacetoxy-2-trichloromethylphthalide (ALIMCHANDANI and MELDRUM), 206.

$C_{15}H_{13}O_2N_3$ 3:5-Dimethyl*iso*oxazole-4-azo-β-naphthol (MORGAN and BURGESS), 702.

$C_{15}H_{13}O_4N_3$ 4-Nitro-2-carbethoxyazobenzene (KENNER and WITHAM), 1056.

$C_{15}H_{13}O_5N_3$ 6-Nitro-*m*-xylene-4-azosalicylic acid (PEARMAN), 718.

$C_{15}H_{13}N_4Br$ 5-Amino-4-(2′-amino-5′-bromophenyl)-2-phenylglyoxaline, and its salts (FARGHER), 160.

$C_{15}H_{14}ON_4$ 3:5-Dimethyl*iso*oxazole-4-azo-β-naphthylamine (MORGAN and BURGESS), 703.

$C_{15}H_{15}ON$ β-Amino-β-phenylpropiophenone (McKENZIE and BARROW), 69.

$C_{15}H_{15}O_3N_3$ *p*-Nitrobenzaldoxime-*N*-*p*-ethylaminophenyl ether (BARROW and GRIFFITHS), 215.

$C_{15}H_{15}O_3N_3$ *p*-Nitrobenzaldoxime-*N*-*p*-dimethylaminophenyl ether (BARROW and GRIFFITHS), 214.

$C_{15}H_{15}O_4N$ β-Carbethoxy-α-methylvinyl indole-2-carboxylate (Kermack, Perkin, and Robinson), 1629.

$C_{15}H_{15}O_4N_3$ Nitrocarbethoxyhydrazobenzenes (Kenner and Witham), 1056.

$C_{15}H_{16}ON_2$ β-Amino-*p*-phenylpropionanilide (McKenzie and Barrow), 71.

$C_{15}H_{17}O_2N$ 4-Dimethylamino-2-hydroxybenzhydrol, and its salts (Krishna and Pope), 287.

$C_{15}H_{17}O_2N_3$ 3:5-Dicyano-2:6-diketo-4-*cyclo*hexenylmethyl-4-methylpiperidine (Kon and Stevenson), 92.

$C_{15}H_{17}O_5N_3$ Antipyrylaminodiacetic acid, and its salts, additive compounds of, with neutral salts (Fargher and King), 292.

$C_{15}H_{18}ON_2$ 6-Acetylamino-9-methyltetrahydrocarbazole (Perkin and Plant), 1835.

$C_{15}H_{18}N_4Cl_2$ 3:7-Diamino-2:8-dimethylphenazine methochloride (Cohen and Crabtree), 2067.

$C_{15}H_{19}ON$ Anilide of lactonic acid $C_{10}H_{14}O_4$ (Birch, Gough, and Kon), 1327.

$C_{15}H_{19}O_3N$ Anilic acid from *cyclo*-hexane-1-acetic-1-carboxylic acid (Norris and Thorpe), 1207.

$C_{15}H_{19}O_3N_3$ Semicarbazone of *ac*-1-keto-3-ethyltetrahydronaphthyl-3-acetic acid (Kon and Stevenson), 92.

$C_{15}H_{20}O_3N_2$ Indole-2-carboxyacetalylamide (Kermack, Perkin, and Robinson), 1626.

$C_{15}H_{21}O_2N_3$ Eserine, degradation of (Stedman), 891.

$C_{15}H_{21}O_6Ga$ Gallium acetylacetone (Morgan and Drew), 1061.

$C_{15}H_{21}O_6In$ Indium acetylacetone (Morgan and Drew), 1062.

$C_{15}H_{23}O_6N$ Ethyl ω- and ω′-cyano-ω-methylmethanetriacetates (Ingold and Perren), 1600, 1868.

15 IV

$C_{15}H_6O_2N_2Br_8$ Dibromomalon-2:4:6-tribromoanilide (Backes, West, and Whiteley), 375.

$C_{15}H_8O_2N_2Br_6$ Dibromomalon-2:4-dibromoanilide (Backes, West, and Whiteley), 374.

$C_{15}H_8O_{10}N_6S_2$ Tetranitrodithiomesoxanilide (Naik), 383.

$C_{15}H_{10}O_2N_2Br_4$ Dibromomalon-*p*-bromoanilide (Backes, West, and Whiteley), 374.

$C_{15}H_{11}O_2N_2Br_3$ Bromomalon-*p*-bromoanilide (Backes, West, and Whiteley), 374.

$C_{15}H_{12}O_2N_2Br_2$ Dibromomalonanilide (Backes, West, and Whiteley), 375.

$C_{15}H_{12}O_2N_2S_2$ Dithiomesoxanilide (Naik), 382.

$C_{15}H_{14}ONCl$ β-*m*-Chlorophenylpropionanilide (Kenner and Witham), 1460.

$C_{15}H_{15}O_2NBr_2$ Dibromo-derivative of 4-dimethylamino-2-hydroxybenzhydrol (Krishna and Pope), 287.

C_{16} Group.

$C_{16}H_{12}O_2$ *o*-Dimethylanthraquinones (Fairbourne), 1573.

$C_{16}H_{14}O_5$ 4′-Hydroxy-2-methoxy-3-methylbenzophenone-6-carboxylic acid, and its silver salt (Simonsen and Rau), 1346.

$C_{16}H_{19}As$ Phenyl-γ-phenylpropylmethylarsine (Burrows and Turner), 431.

$C_{16}H_{26}O_8$ Ethyl *n*-butane-αβγδ-tetracarboxylate (Ingold), 348.
Ethyl carboxymethanetriacetate (Ingold and Powell), 1873.

$C_{16}H_{32}O_2$ Palmitic acid, sodium salt, adsorption by (Laing), 1669.

16 III

$C_{16}H_2O_5N_2$ 9:10-Dinitro-2-ethoxyphenanthrene (HENSTOCK), 61.

$C_{16}H_{11}O_3N_3$ 1-Benzoyl-4(or 5)-nitrophenylglyoxalines (GRANT and PYMAN), 1899.

$C_{16}H_{12}ON_2$ 1-Benzoyl-4(or 5)-phenylglyoxaline (GRANT and PYMAN), 1899.

$C_{16}H_{12}O_2S_2$ Diacetylthianthren (RÂY), 1965.

$C_{16}H_{12}O_8N_2$ Methyl γ-6:6′-dinitrodiphenate (KENNER and STUBBINGS), 599.

$C_{16}H_{13}OBr$ 10-Bromo-2-ethoxyphenanthrene (HENSTOCK), 60.

$C_{16}H_{13}O_3N_4$ Substance from benzenediazonium chloride and 4-*p*-hydroxybenzylhydantoin (SCOTT and COHEN), 671.

$C_{16}H_{14}O_3N_2$ Carbethoxyaminophenanthridone (KENNER and STUBBINGS), 601.

Phenylopiazones (FARGHER and PERKIN), 1743.

$C_{16}H_{15}O_4N$ Anilino-*m*-opianic acid (FARGHER and PERKIN), 1739.

Substance, from anilino-*m*-opianic acid and hydrochloric acid (FARGHER and PERKIN), 1740.

$C_{16}H_{15}O_4N_3$ Benzaldehyde 4-nitro-2-carbethoxyphenylhydrazone (KENNER and WITHAM), 1055.

$C_{16}H_{16}O_3N_2$ *n*-Butyrophenone-3-azoresorcinol (MORGAN and HICKINBOTTOM), 1884.

$C_{16}H_{16}O_5N_4$ 3-Nitro-4-hydroxyphenyl *n*-propyl ketone *p*-nitrophenylhydrazone (MORGAN and HICKINBOTTOM), 1888.

$C_{16}H_{17}O_2N_3$ Phenyl *n*-propyl ketone *p*-nitrophenylhydrazone (MORGAN and HICKINBOTTOM), 1882.

$C_{16}H_{17}O_3N_3$ 3-Hydroxyphenyl *n*-propyl ketone *p*-nitrophenylhydrazone (MORGAN and HICKINBOTTOM), 1885.

$C_{16}H_{17}N_2Cl$ 4-Chlorophenyl *n*-propyl ketone phenylhydrazone (MORGAN and HICKINBOTTOM), 1886.

$C_{16}H_{18}O_2N_2$ 5-Hydroxy-4-methoxy-*o*-tolyl methyl ketone phenylhydrazone (FARGHER and PERKIN), 1733.

$C_{16}H_{18}O_2S_2$ ββ′-Diphenoxydiethyl disulphide (BENNETT), 425.

$C_{16}H_{18}O_3N_2$ *o*- and *p*-Nitrophenyliminocamphor (FORSTER and SAVILLE), 794.

$C_{16}H_{18}O_4S_6$ 3:5:3′:5′-Tetraketo-4:4′-bisdithio-1:1:1′:1′-tetramethyldi*cyclo*hexyl 2:2′-disulphide (NAIK), 1240.

$C_{16}H_{19}ON$ Anilide of *cyclo*pentane*spirocyclo*hexane-3:5-dione (NORRIS and THORPE), 1207.

$C_{16}H_{19}O_4N_3$ *o*- and *p*-Nitrophenylnitrosoaminocamphor (FORSTER and SAVILLE), 793.

$C_{16}H_{19}O_5N_3$ Dinitrophenylaminocamphor (FORSTER and SAVILLE), 792.

$C_{16}H_{19}N_2I$ Phenylbenzylallylazonium iodide, additive compound of thiocarbamide and (SINGH and LAL), 211.

$C_{16}H_{20}O_7N_2$ *N*-Phenylcamphorimidoxime and Phenylnitrosoaminocamphor (FORSTER and SAVILLE), 792.

$C_{16}H_{20}N_4Cl_2$ 3-Amino-7-dimethylamino-2-methylphenazine methochloride (COHEN and CRABTREE), 2058.

$C_{16}H_{21}ON$ Phenylaminocamphor, hydrochloride of (FORSTER and SAVILLE), 791.

$C_{16}H_{21}N_2I$ Phenylbenzylpropylazonium iodide, additive compound of thiocarbamide and (SINGH and LAL), 211.

$C_{16}H_{22}ON_2$ *p*-Aminophenylaminocamphor, and its dihydrochloride (FORSTER and SAVILLE), 794.

$C_{16}H_{22}O_3N_2$ 1-Methylindole-2-carboxyacetalylamide (KERMACK, PERKIN, and ROBINSON), 1637.

Scatole-2-carboxyacetalylamide (KERMACK, PERKIN, and ROBINSON), 1635.

$C_{16}H_{22}O_4N_2$ 6-Methoxyindole-2-carboxyacetalylamide (KERMACK, PERKIN, and ROBINSON), 1633.

16 IV

$C_{16}H_8O_4N_2S$ *N*-Sulphidodiphthalimide (NAIK), 1170.

$C_{16}H_{10}O_3N_2S_2$ 5-Disulphido-1:3-diphenylbarbituric acid (NAIK), 885.

$C_{16}H_{11}ONBr_2$ Dibromo-9-acetylaminophenanthrene (HENSTOCK), 59.

$C_{16}H_{11}O_2N_4Br$ 4-*p*-Bromobenzeneazo-2-phenylglyoxaline-5-carboxylic acid, and its sodium salt (FARGHER), 159.

$C_{16}H_{11}O_3N_2Br$ 5-Bromo-1:3-diphenylbarbituric acid (BACKES, WEST, and WHITELEY), 378.

$C_{16}H_{14}ON_2S$ 2-Acetyl-3-oxy(1)thionaphthenphenylhydrazone (SMILES and MCCLELLAND), 1814.

$C_{16}H_{14}O_2N_2S_2$ Diacetylaminothianthren (RÂY), 1964.

$C_{16}H_{15}O_2N_3Cl_2$ 3:4-Dichlorophenyl *n*-propyl ketone *p*-nitrophenylhydrazone (MORGAN and HICKINBOTTOM), 1889.

$C_{16}H_{15}O_4N_4Cl$ 4-Chloro-3-nitrophenyl *n*-propyl ketone *p*-nitrophenylhydrazone (MORGAN and HICKINBOTTOM), 1888.

$C_{16}H_{16}O_2N_3Cl$ 4-Chloro-3-nitrophenyl *n*-propyl ketone phenylhydrazone (MORGAN and HICKINBOTTOM), 1888.

Chlorophenyl *n*-propyl ketone *p*-nitrophenylhydrazones (MORGAN and HICKINBOTTOM), 1885.

C_{17} Group.

$C_{17}H_8O_8$ Benzophenone-2:4:2′:4′-tetracarboxylic acid ketodilactone (MILLS and NODDER), 2099.

$C_{17}H_{10}O_8$ Benzhydrol-2:4:2′:4′-tetracarboxylic acid lactone (MILLS and NODDER), 2102.

$C_{17}H_{14}O_4$ 1:6-Dimethoxy-2-methylanthraquinone (SIMONSEN and RAU), 1347.

Phenolcitraconein, and its potassium salt (KRISHNA and POPE), 289.

$C_{17}H_{15}As$ Phenyl-α-naphthylmethylarsine (BURROWS and TURNER), 432.

$C_{17}H_{16}O_3$ Eugenol benzoates, melting points of (MCKIE), 777.

$C_{17}H_{16}O_5$ 2:4′-Dimethoxy-3-methylbenzophenone-6-carboxylic acid, and its silver salt (SIMONSEN and RAU), 1347.

$C_{17}H_{16}Br_2$ Hydrocarbon, from petroleum extract of the bromination of phenanthrene (HENSTOCK), 60.

$C_{17}H_{18}O$ Di-*m*-xylyl ketone, preparation of (MILLS and NODDER), 2099.

$C_{17}H_{20}O$ Benzylidene-*dl*-piperitone (READ and SMITH), 784.

$C_{17}H_{26}O_8$ Ethyl *cyclo*pentane-1:2:2:3-tetracarboxylate (PERKIN and ROBINSON), 1397.

17 III

$C_{17}H_6O_6Cl_2$ Acid chloride of benzophenone-2:4:2′:4′-tetracarboxylic acid ketodilactone (MILLS and NODDER), 2100.

$C_{17}H_9O_8Cl_9$ Lactone of 7:8-diacetoxy-2:4-bistrichloromethyl-6-β-trichloro-α-hydroxyethyl-1:3-benzdioxine-5-carboxylic acid (ALIMCHANDANI and MELDRUM), 207.

$C_{17}H_{10}O_4Br_4$ Tetrabromophenolcitraconein (KRISHNA and POPE), 290.

$C_{17}H_{11}N_2Cl$ 10-Chloro-9-methyl-αβ-naphthaphenazine (MORGAN and CHALLENOR), 1540.

$C_{17}H_{12}ON$ Anilide of *cyclo*hexane*spirocyclo*hexane-3:5-dione (NORRIS and THORPE), 1206.

$C_{17}H_{13}O_2N$ Dihydroxynaphthylideneanilines (MORGAN and VINING), 179.

$C_{17}H_{13}O_4N$ β-Phthalimino-β-phenylpropionic acid (MCKENZIE and BARROW), 73.

$C_{17}H_{14}O_3N_2$ 2-Carboxyindole-3-acetanilide (Kermack, Perkin, and Robinson), 1625.

$C_{17}H_{15}OAs$ Phenyl-α-naphthylmethylarsine oxide (Burrows and Turner), 432.

$C_{17}H_{15}O_6N$ Anilino-4:5-dimethoxyphthalonic acid, aniline salt (Fargher and Perkin), 1738.

$C_{17}H_{16}O_5N_2$ 1-Toluene-*p*-sulphonylnaphthylenediaminesulphonic acids, and their sodium salts (Morgan and Grist), 608.

$C_{17}H_{17}O_2N$ 3-Benzoylaminophenyl *n*-propyl ketone (Morgan and Hickinbottom), 1884.

$C_{17}H_{17}O_2As$ Hydroxyphenyl-α-naphthylmethylarsonium hydroxide, bromocamphorsulphonate of (Burrows and Turner), 432.

$C_{17}H_{17}O_4N$ Methyl anilino-*m*-opianate (Fargher and Perkin), 1741.
p-Toluidino-*m*-opianic acid (Fargher and Perkin), 1739.

$C_{17}H_{18}O_2N_2$ Dianilinoacetylacetone (Morgan and Drew), 622.
Malondibenzylamide (Backes, West, and Whiteley), 370.

$C_{17}H_{18}O_4N_2$ αα′-Dihydroxyglutardianilides (Ingold), 323.
Opianic acid phenylmethylhydrazones (Fargher and Perkin), 1743.

$C_{17}H_{19}ON$ Benzoyl-*n*-butylaniline (Mills, Harris, and Lambourne), 1298.

$C_{17}H_{19}O_3N$ 4-Dimethylamino-2-acetoxybenzhydrol (Krishna and Pope), 287.

$C_{17}H_{19}O_3N_3$ *p*-Nitrobenzaldoxime-*N*-*p*-diethylaminophenyl ether (Barrow and Griffiths), 215.

$C_{17}H_{19}N_2Cl$ 6(7)-Chloro-7(6)-methylcamphanoquinoxaline (Morgan and Challenor), 1540.

$C_{17}H_{20}O_5N_6$ Di-*p*-nitrophenylhydrazinoacetylacetone (Morgan and Drew), 621.

$C_{17}H_{21}ON$ Anilinomethylene-epicamphor (Perkin and Titley), 1100.
Benzylidene-*dl*-piperitoneoxime (Read and Smith), 788.

$C_{17}H_{22}IAs$ Phenyl-γ-phenylpropylmethylarsine methiodide (Burrows and Turner), 431.

$C_{17}H_{24}O_3N_2$ 1:3-Dimethylindole-2-carboxyacetalylamide (Kermack, Perkin, and Robinson), 1637.

$C_{17}H_{25}O_8N$ Ethyl α-cyano-*n*-butane-αβγδ-tetracarboxylate (Ingold), 348.

17 IV

$C_{17}H_{12}O_3NCl$ β-Phthalimino-β-phenylpropionyl chloride (McKenzie and Barrow), 78.

$C_{17}H_{12}O_{10}N_6S_2$ Tetranitrodithiomesoxotoluidides (Naik), 1235.

$C_{17}H_{13}O_2N_2Br$ Dihydroxynaphthaldehyde phenylhydrazones (Morgan and Vining), 178.

$C_{17}H_{14}O_2N_2Br_4$ Dibromomalonbromotoluidides (Backes, West, and Whiteley), 376.

$C_{17}H_{14}O_3N_2S_2$ αγ-Disulphidoacetonedicarboxydianilide (Naik), 1240.

$C_{17}H_{15}O_2N_2Br_3$ Bromomalon-4-bromo-*o*-toluidide (Backes, West, and Whiteley), 377.

$C_{17}H_{16}O_2N_2Br_2$ Dibromomalondibenzylamide (Backes, West, and Whiteley), 371.
Dibromomalon-*p*-toluidide (Backes, West, and Whiteley), 376.
Malonbromotoluidides (Backes, West, and Whiteley), 376.

$C_{17}H_{16}O_2N_2S$ Toluene-*p*-sulphonyl-1:4-naphthylenediamine (Morgan and Grist), 604.

$C_{17}H_{16}O_2N_2S_2$ Dithiomesoxodibenzylamide (Naik), 384.
Dithiomesoxotoluidides (Naik), 1235.

$C_{17}H_{16}O_4NCl$ Phenylchloroacetyl-*l*-tyrosine (Shimomura and Cohen), 1824.

$C_{17}H_{16}O_4N_5Cl$ Diacetyl derivative of 4′-nitrobenzene-5-azo-6-chloro-2:4-tolylenediamine (Morgan and Jones), 188.

$C_{17}H_{17}O_2N_2Br$ Bromomalondibenzylamide (Backes, West, and Whiteley), 370.

Bromomalon-*p*-toluidide (Backes, West, and Whiteley), 376.

$C_{17}H_{17}O_2N_4Cl$ Diacetyl derivative of benzene-5-azo-6-chloro-2:4-tolylenediamine (Morgan and Jones), 188.

C_{18} Group.

$C_{18}H_{16}O_5$ Piperonylidene derivative of 5-hydroxy-4-methoxy-*o*-tolyl methyl ketone (Fargher and Perkin), 1733.

$C_{18}H_{18}O_3$ Benzylidene derivative of 4:5-dimethoxy-*o*-tolyl methyl ketone (Fargher and Perkin), 1732.

$C_{18}H_{18}O_5$ Methyl 2:4′-dimethoxy-3-methylbenzophenone-6-carboxylate (Simonsen and Rau), 1346.

$C_{18}H_{20}O_3$ Benzoyloxymethylene-epicamphor (Perkin and Titley), 1099.

$C_{18}H_{30}O_2$ Linolenic acid, and its salts (Coffey), 1306; oxidation of (Coffey), 1409.

$C_{18}H_{32}O_2$ Linolic acid, oxidation of (Coffey), 1408.

18 III

$C_{18}H_{12}O_8N_4$ "Diacetylhydrazide" of γ-6:6′-dinitrodiphenic acid (Kenner and Stubbings), 600.

$C_{18}H_{14}ON_2$ Cinnamoylaminoquinolines (Hamer), 1437.

$C_{18}H_{15}O_4N$ Methyl β-phthalimino-β-phenylpropionate (McKenzie and Barrow), 74.

$C_{18}H_{15}O_6Cl_3$ βββ-Trichloro-4:4′-dihydroxy-αα-di-*m*-tolylethane-5:5′-dicarboxylic acid, and its calcium salt (Alimchandani and Meldrum), 209.

$C_{18}H_{16}O_6N_2$ γ-6:6′-Diacetylaminodiphenic acid (Kenner and Stubbings), 600.

$C_{18}H_{16}O_8N_2$ Ethyl γ-6:6′-dinitrodiphenate (Kenner and Stubbings), 599.

$C_{18}H_{16}O_8N_4$ Dinitro-2:3:6:7-tetramethoxyanthraquinonedi-imide (Keffler), 1481.

$C_{18}H_{17}O_6N$ *p*-Toluidino-4:5-dimethoxyphthalonic acid, *p*-toluidine salt (Fargher and Perkin), 1739.

$C_{18}H_{17}O_6N_3$ Diacetyl derivative of 6-nitro-*m*-xylene-4-azoresorcinol (Pearman), 717.

$C_{18}H_{18}O_4N_2$ 2:3:6:7-Tetramethoxyanthraquinonedi-imide (Keffler), 1480.

$C_{18}H_{18}O_6N_4$ Ethylidenebis-*p*-nitrophenylacetamide (Gupta), 302.

$C_{18}H_{18}O_7N_2$ *o*-Azoxy-*p*-methoxyphenylacetic acid (Kermack, Perkin, and Robinson), 1631.

$C_{18}H_{18}N_4Cl_2$ Tetramethylenebis-2-chloro-4:5-diaminotoluene (Morgan and Challenor), 1541.

$C_{18}H_{18}IAs$ Phenyl-α-naphthylmethylarsine methiodide (Burrows and Turner), 432.

$C_{18}H_{20}O_2N_2$ 6:6′-Diacetylamino-2:2′-ditolyl (Kenner and Stubbings), 600.

Methylmalonotoluidides (Naik), 1238.

$C_{18}H_{21}O_2N_3$ *m*-4-Xylyl-*n*-propyl ketone *p*-nitrophenylhydrazone (Morgan and Hickinbottom), 1889.

$C_{18}H_{21}N_4Cl$ 3-Amino-2-methyl-*N*-methyltetrahydroquinolinophenazine methochloride (Cohen and Crabtree), 2065.

$C_{18}H_{23}O_2N$ Phenylacetylaminocamphor (Forster and Saville), 791.

$C_{18}H_{25}O_2Cl$ *l*-Menthyl *dl*-phenylchloroacetate (Shimomura and Cohen), 1818.

$C_{18}H_{25}O_2Br$ *l*-Menthyl *dl*-phenylbromoacetate (SHIMOMURA and COHEN), 1820.

$C_{18}H_{27}O_8N$ Ethyl ω-cyano-ω′-carboxy-ω″-methylmethanetriacetate (INGOLD and PERREN), 1599.

$C_{18}H_{30}O_2Br_6$ Hexabromostearic acid, and its salts (COFFEY), 1306.

$C_{18}H_{41}O_3N_3$ Tri(diethylaminomethyl) glyceryl ether (MCLEOD and ROBINSON), 1473.

18 IV

$C_{18}H_{16}O_6N_2S_2$ ββ′-Di-*p*-nitrobenzoyldiethyl disulphide (BENNETT and WHINCOP), 1861.

$C_{18}H_{24}ONCl$ Phenylchloroaceto-*d*-bornylamide (SHIMOMURA and COHEN), 1823.

$C_{18}H_{26}ONCl$ Phenylchloroaceto-*l*-menthylamide (SHIMOMURA and COHEN), 1823.

C_{19} Group.

$C_{19}H_{13}N$ 5-Phenylacridine, picrates of (BASSETT and SIMMONS), 417.

$C_{19}H_{14}O_6$ Acetyl derivative of 1:6-dimethoxy-2-methylanthraquinone (SIMONSEN and RAU), 1347.

$C_{19}H_{16}O_3$ Fluoran derivative of citraconic anhydride (KRISHNA and POPE), 291.

$C_{19}H_{18}O_4$ Phenolcitraconein dimethyl ether (KRISHNA and POPE), 290.

$C_{19}H_{20}O_6$ 4:6:3′:4′-Tetramethoxy-3-phenylchroman-2-one (NIERENSTEIN), 167.

$C_{19}H_{22}O_6$ 2-Hydroxy-4:6:3′:4′-tetramethoxy-3-phenylchroman (NIERENSTEIN), 168.

$C_{19}H_{26}O_3$ *l*-Bornyl α-hydroxy-β-phenylpropionates (WREN and WRIGHT), 802.

$C_{19}H_{28}O_3$ *l*-Menthyl-*d*-atrolactinate (WREN and WRIGHT), 800.

l-Menthyl-*l*-α-hydroxy-β-phenylpropionate (WREN and WRIGHT), 802.

$C_{19}H_{36}O_{11}$ Hexamethyl methylcellobioside (HAWORTH and HIRST), 198.

19 III

$C_{19}H_{14}NBr$ Anthranylpyridinium bromide (+ H_2O) (BARNETT and COOK), 907.

$C_{19}H_{15}ON$ Anthranylpyridinium hydroxide, salts of (BARNETT and COOK), 907.

$C_{19}H_{16}ON_2$ Cinnamoylaminoquinaldines (HAMER), 1437.

$C_{19}H_{16}O_4N_2$ Anhydride of 2-carboxyindole-3-acetanilide and acetic acid (KERMACK, PERKIN, and ROBINSON), 1625.

$C_{19}H_{18}ON_2$ 6-Benzoylaminotetrahydrocarbazole (PERKIN and PLANT), 1833.

$C_{19}H_{18}O_3N_2$ *cyclo*Pentanone-3:4-dicarboxyanilide (INGOLD), 350.

$C_{19}H_{19}O_2N$ 4′-Dimethylamino-2-hydroxydistyryl ketone, and its additive products (HEILBRON and BUCK), 1500, 1515.

$C_{19}H_{20}O_3N_2$ Acetonedicarboxyditoluidides (NAIK), 1241.

$C_{19}H_{20}O_4N_2$ Dianilic acid from methanetriacetic acid (INGOLD), 353.

$C_{19}H_{22}O_3N_2$ Hydroxylamino-derivative of 4′-dimethylamino-2-hydroxydistyryl ketone (HEILBRON and BUCK), 1518.

$C_{19}H_{22}O_4N_2$ αα′-Dihydroxyglutardi-*p*-toluidides (INGOLD), 323.

$C_{19}H_{23}O_3N_3$ Hydroxylamino-derivative of 4′-dimethylamino-2-hydroxydistyryl ketoxime (HEILBRON and BUCK), 1518.

p-Nitrobenzaldoxime-*N*-*p*-di-*n*-propylaminophenyl ether (BARROW and GRIFFITHS), 215.

$C_{19}H_{25}O_5N_3$ Ethyl antipyrylaminodiacetate (FARGHER and KING), 297.

$C_{19}H_{27}O_2Br$ *l*-Menthyl *dl*-α-bromo-β-phenylpropionate (SHIMOMURA and COHEN), 1821.

19 IV

$C_{19}H_{16}ONBr_3$ Anthranylpyridinium perbromide (BARNETT and COOK), 907.

$C_{19}H_{17}ON_2I$ Cinnamoylaminoquinoline methiodides (HAMER), 1437.

$C_{19}H_{18}O_3N_2S_2$ αγ-Disulphidoacetonedicarboxyditoluidides (NAIK), 1241.

$C_{19}H_{19}ON_4I$ Phenylhydrazine derivative (+ $3H_2O$) of substance $C_7H_7O_2I$ (COLLIE and REILLY), 1554.

$C_{19}H_{20}O_4NCl$ Ethyl ester of phenylchloroacetyl-*l*-tyrosine (SHIMOMURA and COHEN), 1824.

C_{20} Group.

$C_{20}H_{10}O_4$ Dinaphtha-1:7:1′:7′-diquinone (MORGAN and VINING), 1707.

$C_{20}H_{13}N_3$ Aminophenanthraphenazines (WATSON and DUTT), 1215.

$C_{20}H_{14}O_4$ Phenolphthalein, preparation of (WARD), 850.
 1:7:1′:7′-Tetrahydroxydinaphthyl (MORGAN and VINING), 1712.

$C_{20}H_{14}N_4$ Diaminophenanthraphenazines (WATSON and DUTT), 1215.

$C_{20}H_{15}N_5$ 2:7:11-Triaminophenanthraphenazine, and its hydrochloride (WATSON and DUTT), 1217.

$C_{20}H_{16}O$ Triphenylvinyl alcohol, constitution of (MCKENZIE and BOYLE), 1131.

$C_{20}H_{16}N_4$ 2:7-Diaminodihydrophenanthraphenazine, and its hydrochloride (WATSON and DUTT), 1216.

$C_{20}H_{17}N$ 9-Phenylamino-9:10-dihydroanthracene (BARNETT and COOK), 909.

$C_{20}H_{18}O_9$ *m*-Opianic anhydride (FARGHER and PERKIN), 1742.

$C_{20}H_{24}O_7$ ω-Hydroxy-3:4:2′:4′:6′-pentamethoxy-αα-diphenylpropan-β-one (NIERENSTEIN), 166.

$C_{20}H_{24}N_4$ Base, from formaldehyde and 4:6-diamino-*m*-xylene (PEARMAN), 720.

$C_{20}H_{38}O_{11}$ Heptamethyl methylcellobioside (HAWORTH and HIRST), 199.

20 III

$C_{20}H_{10}Cl_2S_2$ Substance, from α-chloronaphthalene and sulphur chloride (RAY), 1964.

$C_{20}H_{12}O_4N_2$ Dinaphtha-1:7:1′:7′-diquinonedioxime (MORGAN and VINING), 1711.

$C_{20}H_{14}O_2N_2$ 2:7-Dihydroxydihydrophenanthraphenazine (WATSON and DUTT), 1217.

$C_{20}H_{14}ClBi$ Di-α-naphthylchlorobismuthine (CHALLENGER and ALLPRESS), 918.

$C_{20}H_{16}O_2N_2$ 9-Nitrophenylamino-9:10-dihydroanthracenes (BARNETT and COOK), 909.

$C_{20}H_{18}O_2N_2$ *n*-Butyrophenoneazo-β-naphthols (MORGAN and HICKINBOTTOM), 1884.

$C_{20}H_{19}ON_3$ *n*-Butyrophenone-3-azo-β-naphthylamine (MORGAN and HICKINBOTTOM), 1884.

$C_{20}H_{19}O_2N_3$ 6-Acetylamino-*m*-xylene-4-azo-β-naphthol (PEARMAN), 718.

$C_{20}H_{20}BrAs$ Phenyl-α-naphthylmethylallylarsonium bromide (BURROWS and TURNER), 434.

$C_{20}H_{21}O_2N$ 4′-Dimethylamino-2-methoxydistyryl ketone, and its additive compounds (HEILBRON and BUCK), 1509.

$C_{20}H_{22}O_4N_2$ 2:6-Dimethoxy-3:7-diethoxyanthraquinonedi-imide (KEFFLER), 1482.

$C_{20}H_{24}ON_2$ 4-Amino-1-naphthylaminocamphor, and its hydrochloride (Forster and Saville), 797.

$C_{20}H_{24}O_2N_2$ Quinine, hexabromostearate of (Coffey), 1309.

$C_{20}H_{25}O_3N_3$ Hydroxylamino-derivative of 4′-dimethylamino-2-methoxydistyryl ketoxime (Heilbron and Buck), 1518.

20 IV

$C_{20}H_{16}O_2N_2S$ Naphthalene-α- and -β-sulphonyl-1:4-naphthylenediamine (Morgan and Grist), 605.

$C_{20}H_{19}ON_2I$ Cinnamoylaminoquinaldine methiodides (Hamer), 1437.

C_{21} Group.

$C_{21}H_{16}O_5$ Resorcinolcoumarein (Krishna), 1424.

$C_{21}H_{16}O_8$ Ethyl benzophenone-2:4:2′:4′-tetracarboxylate ketodilactone (Mills and Nodder), 2101.

$C_{21}H_{18}O_6$ Diacetyl derivative of phenolcitraconein (Krishna and Pope), 290.

$C_{21}H_{19}N$ 9-Phenylmethylamino-9:10-dihydroanthracene (Barnett and Cook), 912.

9-Tolylamino-9:10-dihydroanthracenes (Barnett and Cook), 910.

$C_{21}H_{20}O_5$ Phenolcoumarein, and its salts (Krishna), 1420.

$C_{21}H_{21}Bi$ Tri-*m*-tolylbismuthine (Challenger and Allpress), 920.

$C_{21}H_{22}O_4$ Phenolcitraconein diethyl ether (Krishna and Pope), 291.

$C_{21}H_{28}O_4$ Methylenebis*cyclo*pentane*spirocyclo*hexane-3:5-dione (Norris and Thorpe), 1208.

21 III

$C_{21}H_{12}O_3Br_4$ Tetrabromophenolcoumarein (Krishna), 1424.

$C_{21}H_{12}O_5Br_4$ Tetrabromoresorcinolcoumarein (Krishna), 1425.

$C_{21}H_{15}N_2Cl$ 5-Chloro-2:3-diphenyl-6-methylquinoxaline (Morgan and Glover), 1706.

6(7)-Chloro-2:3-diphenyl-7(6)-methylquinoxaline (Morgan and Challenor), 1539.

$C_{21}H_{16}O_3Br_2$ Phenoldibromocoumarein (Krishna), 1424.

$C_{21}H_{17}O_2N$ 9-*o*-Carboxyphenylamino-9:10-dihydroanthracene (Barnett and Cook), 910.

$C_{21}H_{19}O_2N$ 6-Dimethylamino-3-hydroxy-9-phenylxanthen (Krishna and Pope), 288.

$C_{21}H_{19}N_2I$ 1:1′-Dimethyl*iso*cyanine iodide (Hamer), 1439.

$C_{21}H_{20}O_4Cl$ Ethyl di-*n*-chlorobenzylmalonate (Kenner and Witham), 1460.

$C_{21}H_{20}N_3I$ Amino-1:1′-dimethyl*iso*cyanine iodides (Hamer), 1443.

$C_{21}H_{21}O_3N$ Acetyl derivative of 4′-dimethylamino-2-hydroxydistyryl ketone (Heilbron and Buck), 1509.

$C_{21}H_{22}O_2N_2$ Strychnine, hexabromostearate of (Coffey), 1309.

$C_{21}H_{23}ON$ β-Naphthylaminomethylene-epicamphor (Perkin and Titley), 1100.

$C_{21}H_{24}ON_2$ *pp*′-Tetramethyldiaminodistyryl ketone (Heilbron and Buck), 1514.

$C_{21}H_{24}O_2N_4$ Semicarbazone of 4′-dimethylamino-2-methoxydistyryl ketone (Heilbron and Buck), 1519.

$C_{21}H_{27}ON$ 2-Benzoylamino-1:4-di-*n*-butylbenzene (Morgan and Hickinbottom), 1893.

$C_{21}H_{27}O_3N_4$ Semicarbazide derivative of 4′-dimethylamino-2-hydroxydistyryl ketone semicarbazone (Heilbron and Buck), 1519.

C_{22} Group.

$C_{22}H_{10}O_4$ 1:2-Phthaloylanthraquinone (Fairbourne), 1580.

$C_{22}H_{34}Si_2$ *dl*-Diphenyldiethyldipropylsilicoethane (Kipping), 648.

22 III

$C_{22}H_{16}ON_2$ 1-Methoxy-2-methylphenanthraphenazine (Simonsen and Rau), 1343.

$C_{22}H_{19}O_2N$ β-Benzoylamino-β-phenylpropiophenone (McKenzie and Barrow), 73.

$C_{22}H_{21}ON$ 6-Dimethylamino-3-hydroxy-9-phenyl-2-methylxanthen (Krishna and Pope), 288.

$C_{22}H_{21}O_3N$ 4-Dimethylamino-2-benzoyloxybenzhydrol (Krishna and Pope), 288.

$C_{22}H_{22}O_2N_2$ Butyro-2:4-dimethylphenone-5-azo-β-naphthol (Morgan and Hickinbottom), 1890.

$C_{22}H_{24}O_4S_8$ 1:1′-Di*cyclo*hexane*spiro*-3:5:3′:5′-tetraketo-4:4′-bisdithiodi*cyclo*hexylene-2:2′:6:6′-bisdisulphide (Naik), 1240.

$C_{22}H_{24}O_3N_4$ *p*-Nitrobenzeneazophenylaminocamphor (Forster and Saville), 796.

$C_{22}H_{26}O_4N_2$ Mitraversine, and its hydrochloride (Field), 891.

$C_{22}H_{31}O_5N$ Mitragynine, and its salts (Field), 888.

22 IV

$C_{22}H_{18}O_3N_2Cl_2$ Ethyl αα-bis-3-chloro-2-cyanobenzylacetoacetate (Kenner and Witham), 1459.

$C_{22}H_{24}O_4N_2S_2$ Di-*p*-toluenesulphonyl-4:6-diamino-*m*-xylene (Pearman), 719.

$C_{22}H_{25}O_4N_3S$ *p*-Sulphobenzeneazophenylaminocamphor (Forster and Saville), 796.

$C_{22}H_{26}O_4N_4S_2$ Methylmalonomono-*o*-toluidide disulphide (Naik), 1238.

C_{23} Group.

$C_{23}H_{32}O_4$ Methylenebis*cyclo*hexane*spirocyclo*hexane-3:5-dione (Norris and Thorpe), 1206.

23 III

$C_{23}H_{12}O_6S_2$ Methylene bis-(1)thionaphtha-4-oxycoumarin (Smiles and McClelland), 1816.

$C_{23}H_{17}O_3N$ β-Phthalimino-β-phenylpropiophenone (McKenzie and Barrow), 75.

$C_{23}H_{18}O_3N_2$ β-Phthalimino-β-phenylpropionanilide (McKenzie and Barrow), 74.

$C_{23}H_{19}O_4N$ β-Benzoyl-α-phenylethylphthalamic acid (McKenzie and Barrow), 75.

$C_{23}H_{22}O_2N_2$ Benzylidenebisphenylacetamide (Gupta), 800.

$C_{23}H_{24}O_3N_2$ Benzoyl derivative of phenylcamphorimide (Forster and Saville), 792.

$C_{23}H_{26}O_2N_2$ *p*-Benzoylaminophenylaminocamphor (Forster and Saville), 795.

23 IV

$C_{23}H_{10}O_{15}N_8S$ Hexanitro-derivative of oxythiomesoxo-α-naphthylamide (Naik), 1236.

$C_{23}H_{12}O_{10}N_6S_2$ Tetranitrodithiomesoxonaphthylamides (Naik), 1236.

$C_{23}H_{16}O_2N_2S_2$ Dithiomesoxonaphthylamides (Naik), 1236.

$C_{23}H_{22}ON_3I$ Acetylamino-1:1′-dimethyl*iso*cyanine iodides (Hamer), 1441.

C_{24} Group.

$C_{24}H_{16}N_2$ Dicarbazyls, isomeric (PERKIN and TUCKER), 221.

$C_{24}H_{19}N$ 9-β-Naphthylamino-9:10-dihydroanthracene (BARNETT and COOK), 911.

$C_{24}H_{24}O_4$ Phenolcoumarein trimethyl ether (KRISHNA), 1423.

$C_{24}H_{28}Si_2$ *dl*-Dibenzyldiethyldipropylsilicoethane (KIPPING), 649.

24 III

$C_{24}H_{20}N_2Br_2$ 9:10-Dihydroanthraquinyldipyridinium dibromide (BARNETT and COOK), 904.

$C_{24}H_{20}N_2Br_6$ 9:10-Dihydroanthraquinyldipyridinium perbromide (BARNETT and COOK), 905.

$C_{24}H_{22}O_2N_2$ 9:10-Dihydroanthraquinyldipyridinium dihydroxide, salts of (BARNETT and COOK), 906.

$C_{24}H_{22}BrAs$ Phenyl-α-naphthylbenzylmethylarsonium bromide (BURROWS and TURNER), 435.

$C_{24}H_{22}IAs$ Phenyl-α-naphthylbenzylmethylarsonium iodide (BURROWS and TURNER), 436.

$C_{24}H_{23}OAs$ Phenyl-α-naphthylbenzylmethylarsonium hydroxide, salts of (BURROWS and TURNER), 435.

$C_{24}H_{24}O_2N_2$ Phenylethylidenebisphenylacetamide (GUPTA), 302.

$C_{24}H_{24}O_3N_2$ Anisylidenebisphenylacetamide (GUPTA), 301.

24 IV

$C_{24}H_{16}O_4N_4S$ Diamino-15-hydroxyphenanthranaphthazine-13-sulphonic acids (WATSON and DUTT), 1218.

$C_{24}H_{17}ON_3S$ 1-Phenyl-5-methylbenzothiazole-4-azo-β-naphthol (MORGAN and WEBSTER), 1073.

$C_{24}H_{38}O_6S_2Si_2$ Dibenzyldiethyldipropylsilicoethanedisulphonic acid, *l*-menthylamine salt (KIPPING), 652.

C_{25} Group.

$C_{25}H_{22}O_6$ Diacetyl derivative of phenolcoumarein (KRISHNA), 1423.

25 III

$C_{25}H_{21}ON$ 8-Dimethylamino-11-phenyl-β-naphthaxanthen (KRISHNA and POPE), 288.

$C_{25}H_{23}O_3As$ Homopiperonylphenyl-α-naphthylmethylarsonium hydroxide, salts of (BURROWS and TURNER), 434.

$C_{25}H_{24}O_2N_2$ Cinnamylidenebisphenylacetamide (GUPTA), 301.

$C_{25}H_{25}ON_3$ 4′-Dimethylamino-2-hydroxydistyryl ketone phenylhydrazone (HEILBRON and BUCK), 1519.

$C_{25}H_{26}O_5N_2$ 4:6:3′:4′-Tetramethoxy-3-phenylchroman-2-one phenylhydrazone (NIERENSTEIN), 167.

25 IV

$C_{25}H_{22}OBrAs$ Phenacylphenyl-α-naphthylmethylarsonium bromide (BURROWS and TURNER), 434.

$C_{25}H_{22}O_2BrAs$ Homopiperonylphenyl-α-naphthylmethylarsonium bromide (BURROWS and TURNER), 434.

C_{26} Group.

$C_{26}H_{20}S_2$ Dibenzylthianthren (RÂY), 1965.

$C_{26}H_{21}N$ 9-Diphenylamino-9:10-dihydroanthracene (BARNETT and COOK), 912.

$C_{26}H_{21}N_3$ 9-*p*-Benzeneazophenylamino-9:10-dihydroanthracene (BARNETT and COOK), 911.

26 III

$C_{26}H_{18}O_6N_4$ Dianilide of γ-6:6′-dinitrodiphenic acid (KENNER and STUBBINGS), 599.

$C_{26}H_{20}N_4S_2$ 3:6-Dithio-1:2:4:5-tetraphenylhexahydro-1:2:4:5-tetrazine (NAIK), 1169.

$C_{26}H_{27}ON_3$ 4′-Dimethylamino-2-methoxydistyryl ketone phenylhydrazone, and its pyridine additive compound (HEILBRON and BUCK), 1520.

$C_{26}H_{34}O_2N_2$ Camphorylaminophenyliminocamphor (FORSTER and SAVILLE), 795.

26 IV

$C_{26}H_{20}O_2N_2S_3$ Trisulphidobisbenzanilide (NAIK), 1169.

$C_{26}H_{22}O_4N_4S_2$ Benzene-1:3-disulphonylbis-1:4-naphthylenediamine (MORGAN and GRIST), 606.

$C_{26}H_{22}O_6N_6S_2$ 2:7-Diaminophenanthraquinonediphenylhydrazone-*pp*′-disulphonic acid (WATSON and DUTT), 1221.

$C_{26}H_{27}O_4N_3S$ *p*-Sulphobenzeneazonaphthylaminocamphor (FORSTER and SAVILLE), 797.

C_{27} Group.

$C_{27}H_{13}O_8Cl_9$ Lactone of 7:8-dibenzoyloxy-2:4-bistrichloromethyl-6-β-trichloro-α-hydroxyethyl-1:3-benzdioxine-5-carboxylic acid (ALIMCHANDANI and MELDRUM), 207.

C_{28} Group.

$C_{28}H_{22}O_8$ 1:7:1′:7′-Tetra-acetoxydinaphthyl (MORGAN and VINING), 1713.

28 III

$C_{28}H_{23}O_3N$ 6-Dimethylamino-3-benzoyloxy-9-phenylxanthen (KRISHNA and POPE), 288.

$C_{28}H_{23}N_4Cl$ 2:7-Diamino-11:4′-dimethylflavinduline chloride (WATSON and DUTT), 1219.

$C_{28}H_{24}O_4N_4$ Tetra-acetyl derivative of 2:7-diaminodihydrophenanthraphenazine (WATSON and DUTT), 1217.

28 IV

$C_{28}H_{19}O_4N_4Cl$ 2:7-Dinitro-11:4′-dimethylflavinduline chloride (WATSON and DUTT), 1218.

C_{30} Group.

$C_{30}H_{36}O_2N_2$ Camphoryl-1-aminonaphthyl-4-iminocamphor (FORSTER and SAVILLE), 798.

30 IV

$C_{30}H_{24}O_4N_4S_2$ Naphthalenedisulphonylbis-1:4-naphthalenediamines (MORGAN and GRIST), 606.

$C_{30}H_{26}ON_2I$ Cinnamoylamino-1:1′-dimethyl*iso*cyanine iodides (HAMER), 1440.

C_{31} Group.

$C_{31}H_{22}O_6$ Dibenzoyl derivative of phenolcitraconein (KRISHNA and POPE), 290.

C_{32} Group.

$C_{32}H_{37}O_2N_3$ *pp*′-Bisiminocamphordiphenylamine (B. K. and M. SINGH and LAL), 1975.

$C_{32}H_{40}O_2N_2$ *pp*′-Diphenylenebisaminocamphor (B. K. and M. SINGH and LAL), 1974.

32 IV

$C_{32}H_{30}O_4N_4S_2$ Methylmalonanilide disulphide (Naik), 384.

C_{34} Group.

$C_{34}H_{26}O_2$ Substance, from magnesium phenyl bromide and diphenylchloroacetyl chloride (McKenzie and Boyle), 1138.

34 III

$C_{34}H_{40}O_2N_2$ *oo'*-Ditolylenebisiminocamphor (B. K. and M. Singh and Lal), 1973.

$C_{34}H_{40}O_4N_2$ *oo'*-Dimethoxydiphenylenebisiminocamphor (B. K. and M. Singh and Lal), 1974.

34 IV

$C_{34}H_{22}O_{10}N_6S_2$ Phenanthraquinonebis-(2')-azo-7'-amino-1'-hydroxynaphthalene-3'-sulphonic acids (Watson and Dutt), 1219.

$C_{34}H_{34}O_4N_2S_2$ Malondimethylanilide disulphide (Naik), 384.

C_{36} Group.

$C_{36}H_{26}O_{28}N_{16}S_2$ Dodecanitro-derivative of methylmalono-*p*-toluidide disulphide (Naik), 1238.

$C_{36}H_{38}O_4N_4S_2$ Methylmalonotoluidide disulphides (Naik), 1238.

C_{40} Group.

$C_{40}H_{27}O_8N_9S_2$ 11-Aminophenanthraphenazine-2:7-bis-(2')-azo-7'-amino-1'-hydroxynaphthalene-3'-sulphonic acid (Watson and Dutt), 1220.

$C_{40}H_{28}O_6N_8S_2$ Dihydrophenanthraphenazine-2:7-bis-(2')-azonaphthionic acid (Watson and Dutt), 1220.

C_{42} Group.

$C_{42}H_{30}O_7$ Tribenzoyl derivative of phenolcoumarein (Krishna), 1423.

C_{44} Group.

$C_{44}H_{26}O_{16}N_{16}$ Dinaphtha-1:7:1':7'-diquinonetetra-2:4-dinitrophenylhydrazone (Morgan and Vining), 1712.

$C_{44}H_{48}O_2N_6$ *pp*-Diphenylenebisazophenylaminocamphor (Forster and Saville), 797.

C_{48} Group.

$C_{48}H_{40}OSi_4$ Octaphenylsilicotetrane oxide (Kipping and Sands), 840.

$C_{48}H_{40}O_2Si_4$ Octaphenylsilicotetrane oxide, rhomboidal (Kipping and Sands), 844.

$C_{48}H_{40}I_2Si_4$ Octaphenyldi-iodosilicotetrane (Kipping and Sands), 830.

ERRATA.

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Page	Line	
1386	6*	*for* “latter” *read* “heat of formation of methane.”

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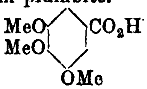
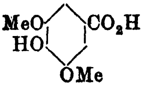
Page	
56	Table V in third column *for* $\left\{\begin{matrix}\text{“}5{\cdot}74\text{”}\\ 6{\cdot}62\\ 5{\cdot}15\end{matrix}\right\}$ *read* $\left\{\begin{matrix}\text{“}57{\cdot}4\text{”}\\ 66{\cdot}2\\ 51{\cdot}5\end{matrix}\right\}$

Page	Line	
83	1*	*for* “$C_5H_{10}O_8N_2S$” *read* “$C_5H_{10}O_5N_2S$.”
345	21*	,, “oxide, a little water” *read* “oxide and a little water.”
348	6*	,, “citronellal” *read* “citronellol.”
350	2	,, “pæonal” *read* “pæonol.”
475	13	,, “*s*” read “*S*.”
475	14	,, “9*ηs*” *read* “9*ηS*.”
475	2*	,, “0·15 cm.” *read* “0·1588 cm.”
476	1	
476	15	
478	10	,, “6·69” *read* “6·69 × 19·4.”
646	26	,, “Mr. E. A. Perren” *read* “Messrs. R. Craven and E. A. Perren.”
646	27	,, “his” *read* “their.”
648	17	,, “*N*/10-$KMnO_4$” *read* “*N*/10-$KMnO_4$ equivalent to.”
648	20	,, “0·03994” *read* “0·03004.”
661	12	,, “sodium sulphate” *read* “sodium hydrogen sulphate.”
832	6	,, “lead acetate” *read* “sodium plumbite.”
965		,, formulæ V. and VI. *read*  and  respectively.
1024	6*	,, “positive” *read* “negative.”
1026	16*	the formula should be “$3K_3[Fe(CN)_6],K_2[Fe(CN)_5H_2O]$.”
1218	19	col. 2 *for* “167·90” *read* “157·90.”
1219		diagram *insert* “y” values at end of horizontal lines, namely, from below upwards “100, 90, 80, 70, 60.”
1270	7*	*for* “$C_{12}H_{12}O_3N_4$” *read* “$C_{18}H_{12}O_3N_4$.”
1276	22	,, “N=17·37. $C_{13}H_{10}O_6N_4$ requires N=17·73” *read* “N=16·35. $C_{20}H_{19}O_6N_5$ requires N=16·47.”
1560	4*	,, “2*β*” *read* “2*θ*.”
1560	13*	,, “2*θ*” *read* “2*β*.”
1560	13*	,, “2*β*” *read* “2*θ*.”

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Page	Line	
29	9*	,, “Shenstone” *read* “Stenhouse.”
30	3*	
50	14	,, “$SrCS_3,8H_2O$” *read* “$SrCS_4,8H_2O$.”
63	4	,, “salts in millimols.” *read* “salts and soaps in millimols. per cent.”
63		in tables I, II, V, VI, and VIII *after* “millimols.” *insert* “per cent.”
64		
65		
66		
68	15	*for* “renewal” *read* “reversal.”

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* From bottom.